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Infrared Spectroscopy of Pristine and Doped Gold Atomic Chains on Vicinal Silicon Surfaces

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Abstract

In this thesis the optical and structural properties of pristine and doped atomic Au chains on Si substrates were investigated. The HCW and LCW surface reconstructions on Si(553) proposed by Song et al. [1] were created. Subsequently the HCWs were doped with additional 0.5 ML Au to create HCWs+0.05 ML. The structure of all three surfaces was analyzed via RHEED, confirming the structural models by Song et al. FTIR measurements at room temperature and down to 20 K showed a continual shift of the plasmonic resonance maximum to smaller wavenumbers of $\omega_{res,shift} = (-140 \pm 10) \text{ cm}^{-1}$ for HCWs, $\omega_{res,shift} = (-66 \pm 5) \text{ cm}^{-1}$ for HCWs+0.05 ML and $\omega_{res,shift} = (-110 \pm 3) \text{ cm}^{-1}$ for LCWs. The HCW's presumably antiferromagnetic ground state could be ruled out as a major factor in this shift. Furthermore C₇₀ was evaporated on the Au/Si(111)-5 × 2 surface, where a decrease in plasmonic signal and shift to higher wavenumbers was observed. For a complete C₇₀ surface coverage, the resonance vanished entirely at room temperature and only lost 20% of its strength at 20 K. This is assumed to be caused by electron transfer from Au chains to C₇₀. We estimate that each C₇₀ molecule absorbs approximately one electron from the Au chains.

Zusammenfassung

In dieser Arbeit wurden die optischen und strukturellen Eigenschaften von reinen und dotierten Au Ketten auf Si Substraten untersucht. Die von von Song et al. [1] vorgeschlagenen HCW und LCW Oberflächenrekonstruktionen of Si(553) wurden hergestellt. Anschließend wurden die HCWs mit zusätzlichen 0.5 ML Au dotiert um HCWs+0.05 ML herzustellen. Die Struktur aller drei Oberflächen wurde mit RHEED untersucht, deren Resultate die Strukturmodelle von Song et al. bestätigen. FTIR Messungen bei Raumtemperatur bis 20 K zeigten eine kontinuierlichen Verschiebung des plasmonischen Resonanzmaximums zu kleineren Wellenzahlen von $\omega_{res,shift} = (-140 \pm 10) \text{ cm}^{-1}$ für HCWs, $\omega_{res,shift} = (-66 \pm 5) \text{ cm}^{-1}$ für HCWs+0.05 ML und $\omega_{res,shift} = (-110 \pm 3) \text{ cm}^{-1}$ für LCWs. Der mutmaßliche antiferromagnetische Grundzustand der HCWs konnte dabei als Hauptursache in dieser Verschiebung des plasmonischen Signals und eine Verschiebung zu höheren Wellenzahlen beobachtet wurde. Für eine komplette Oberflächenbedeckung durch C₇₀ verschwand die Resonanz vollständig bei Raumtemperatur und verlor nur 20% ihrer Stärke bei 20 K. Wir folgern, dass jedes C₇₀ Molekül ein Elektron der Au Ketten aufnimmt.

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1. Introduction

Nanophysics has come to the point where nanostructures can be formed and manipulated in various ways. Graphene, carbon nanotubes and nanowires are just a few of many examples. This thesis specifically deals with the investigation of self assembling atomic gold chains on silicon substrates and the manipulation of their atomic properties via doping of C_{70} and additional gold.

The semiconductor silicon is one of the cheapest and most widely used materials in condensed matter physics. It has a variety of interesting properties, most of them understood and characterized very well due to its abundant usage. We take advantage of this large knowledge base by using stepped silicon surfaces, especially vicinal silicon substrates as template for the metal atoms which form chains along the step edges.

Solid state physics dealing with atomic chains is still an active research area and as such not yet understood in detail. Many methods and approximations used in classical condensed matter theory are not applicable to these chains, considering that they are only several atoms wide and a single atom thick. Yet, this small size makes them very interesting to study, since their properties are dominated by exotic electronic ground states existing only in one dimension [2].

The electronic properties of these wires are also manipulable without massively changing their structure. Coupling to phonons which are mainly involved in scattering processes can be frozen out at lower temperatures [3]. Chemical bonds, such as dangling bonds and adatoms, shift electron energy states and by doing so change their dispersion relation [4]. Dopants like additional gold or C_{70} can increase or decrease the amount of electrons contributing to the electronic properties, resulting in metal insulator transitions [5].

Beside the research of the fundamental properties of these systems there are potential usages of such metallic nanowires in future nano electronics. Since atomic wires represent the smallest possible units for electric current they serve as possible building blocks in future devices like atomic scale memory [6] or as plasmonic waveguides and plasmonic resonators in nanophotonics [7].

2. Theory

2.1 Substrate Structure

Self assembling atomic chains can be manufactured by evaporating sub-monolayer amounts of metals such as gold (Au), silver or indium on a vicinal silicon (Si) surface. They are called vicinal, because they are structurally adjacent to well known surfaces, like the Si(111) reconstruction. The difference consists of slightly different cutting angles, resulting in a step structure. While the flat silicon terrace on the steps hosts the site for the atomic chains to form, the step edges are used to control the chain growth.

The two surface structures relevant to this report are gold chains on the Si(553) and Si(111) surfaces. In Figure 2.1 the surface planes in relation to the crystal structure are shown.

To manufacture the Si(111)-1°off surface a 1° miscut towards $[\overline{112}]$ is used. While this still results in a (111) reconstruction, the surface is interrupted at regular intervals by step edges (Figure 2.2). In the following Si(111)-1°off is abbreviated with the original surfaces name Si(111) as is common practice in literature.

Like Si(111), Si(553) can be considered a miscut from the flat Si(111) surface. The significant difference is the much larger angle of 12.3° between the Si(553) surface normal and the surface normal of flat Si(111) [9], which results in much narrower steps (Figure 2.2).

The step structure is necessary as the step edges define a potential barrier that the chains can not pass. Because of this, the preferred direction for chain growth is parallel to the step edges, which form along $[1\overline{10}]$. For Si(111) not all chains grow parallel to $[1\overline{10}]$ though, as the terraces are wide and the so called step bunching effect can make them even wider. When step bunching occurs, several edges migrate toward each other, resulting in one very steep edge and one very wide terrace [11].

Since the Si(111) surface has a threefold symmetry, along which the chains align in the absence of steps, these wide terraces allow the formation of long chains along the other two equivalent directions, $[01\overline{1}]$ and $[\overline{1}01]$. Although the chain growth along those orientations is suppressed in comparison to the $[1\overline{1}0]$ direction (Figure 2.3a), we carefully heat treat the wafer to minimize step bunching. The details of this are explained in section 3.4.



Figure 2.1: Sideway cut of the silicon lattice crystal structure in the (110) plane. The red and blue lines show the planes along which the silicon crystal is cut to create the Si(553) and Si(111)-1° surfaces. Modified from [8].



Figure 2.2: (a) Sketch of the Si(111) step structure. The terrace is very wide compared to the edge height. Modified from [10]. (b) Sketch of the Si(553) step structure. With the same height as the Si(111) steps, but only a tenth of the width, the Si(553) steps are relatively steep. Modified from [10].



Figure 2.3: (a) Depiction of the possible Au chain growth directions on Si(111). [110] is the preferred orientation. Chain formation parallel to $[01\overline{1}]$ and $[\overline{1}01]$ is also possible but suppressed. Modified from [12]. (b) Depiction of the possible Au chain growth directions on Si(553). The chains only grow in the $[1\overline{1}0]$ direction. (c) Schematic of the most used FTIR spectrometer polarizations. The $[1\overline{1}0]$ polarization is parallel to the preferred chain alignments of both surfaces, while the $[11\overline{2}]$ polarization is perpendicular to them.

The narrow terraces of the Si(553) surface do allow nanowire growth only parallel to the edges (Figure 2.3b). Even though step bunching and faceting does occur on the pristine Si(553) surface as well, this has no influence on chain alignment. As soon as the gold atoms start to form chains, they stabilize the Si structure around them and any existing step bunching gets undone. [13]

This anisotropic chain growth can be demonstrated by polarization dependent FTIR measurements. To do so we polarize the IR light beam of our spectrometer either parallel ($[1\overline{10}]$) or perpendicular ($[11\overline{2}]$) to the chains (Figure 2.3c).

2.1.1 Au/Si(111)-5 \times 2

The current model for the formation of gold chains on Si(111) is the so called Kwon-Kangmodel (KK-model) [4] describing the reconstruction of the Au/Si(111)-5 × 2 surface. Its unit cell is depicted in Figure 2.4. These chains are formed when 0.7 monolayers (ML) of Au are deposited on the silicon, where 1 ML corresponds to one Au atom per Si(111) 1 × 1 unit cell or 7.8×10^{14} Au atoms per cm² [14]. Between each gold wire is a chain of silicon honeycombs, which is a distinct feature of many atomic chains on Si and a key factor in their stability [15].

2.1.2 Si(553) - HCW

Since the Si(553) steps are much narrower than the ones of Si(111), the Au/Si(111)-5 \times 2 structure predicted by the KK-model can not be realized as the small terraces impose a different configuration on the Au chains. For an Au coverage of 0.48 ML so called high coverage wires (HCW) form on Si(553) [16] as can be seen in Figure 2.5.

At low temperatures the HCW structure undergoes a phase transition to its presumably antiferromagnetic ground state.¹ In this state every third silicon atom at the step edge has a well defined spin of 1/2. The spin sign alternates along the edge. The polarization also causes these atoms to be slightly downward displaced by 0.3 Å. Because of this effect the periodicity of the 1 × 2 unit cell triples at low temperatures to 1 × 6 [16].

¹Theorist do not yet agree that this antiferromagnetic ground state is the correct explanation for the different phenomenons measured at lower temperatures. Competing theories, like a Peierls Transition [17], are still being refuted. Nevertheless, this spin ordering explains all currently measured data, hence it will be used throughout the rest of this thesis as working hypothesis.



Figure 2.4: (a) Kwon-Kang-model for the unit cell of Au/Si(111)-5 × 2. Birdseye view on the top, sideway cut at the bottom. The red balls represents Au atoms, the gray ones Si. Three rows of Au atoms make up the chain. The dashed line outlines the 5×2 unit cell, which in total encompasses 7 Au atoms. Modified from [4]. (b) $37.5 \text{ nm} \times 75 \text{ nm}$ STM Image of Au/Si(111)-5 × 2. One can see that the orientation of the Au chains is parallel to the the step edge dividing the lighter and darker side of the image. The lighter spots on the chains are Si adatoms which are naturally occurring adsorbates. Modified from [14].



Figure 2.5: (a) Unit cell model of the HCW surface reconstruction. The yellow atoms are gold, all other are silicon. The surface is made up of two alternating chain types, the Au chain at the step terrace and the Si honeycomb chain forming the step edge. The red parallelogram outlines the (1×2) unit cell at RT, while the black one depicts the (1×6) cell after the antiferromagnetic phase transition. $a_1 \approx 0.42$ nm. Modified from [16]. (b) 37.5 nm × 75 nm STM Image of HCWs. The bright stripes are the gold chains. The black spots are the most common defects, a spot of missing Au atoms, two lattice constants wide. Modified from [7].

2.1.3 Si(553) - LCW

Besides the HCW, another notable wire configuration has been found on the Si(553) surface by Song et al. in 2015. This reconstruction is called low coverage wires (LCWs) and forms for an Au coverage of 0.19 ML [1]. LCWs have similar structure and properties to HCWs, yet they are not only a Au/Si(553) surface that is less densely populated with atomic chains as one might expect from the lower Au amount. Instead, LCW's have the intriguing characteristic of forming one continuous Au chain on every second step and a silicon strip in between as shown in Figure 2.6.



Figure 2.6: (a) Unit cell model of the LCW structure. Birdseye view on the top, sideway cut at the bottom. The surface is made up of three different atomic chains. The Au and Si chains are very similar to the HCW surface since the LCW Au chains are made up of 2 alternating strings of Au atoms as well and the Si chain next to them is constructed from honeycombs. Between every step occupied by Au atoms is a 5×5 silicon strip. Modified from [1] (b) $15.5 \text{ nm} \times 30 \text{ nm}$ STM Image of LCWs. The three different chain types are clearly visible as solid black, solid orange and dotted broad yellow lines. Modified from [1].

2.2 Plasmonic Excitations

2.2.1 Basics

The Au chains on Si studied in this thesis exhibit metallic behavior. Their electrons are partially filled and the electrons near the Fermi level lie between the silicon band gap, resulting in minimal electronic interaction between substrate and chain. They can be described as a one dimensional electron gas with weak but significant coupling to the second dimension [18]. In this system collective plasmonic excitations are the dominating effect relevant for this thesis. An oscillating electric field, such as light, can then be used to induce so called localized surface plasmons, if it is polarized parallel to the nanowires. [14]

To investigate these properties we use infrared spectroscopy (IR spectroscopy, IRS).

2.2.2 Excitation by Infrared Light

A typical IR spectrum of atomic Au chains on Si is shown in Figure 2.7



Figure 2.7: Example of typical relative normal transmittance IRS spectra. The red line is the spectrum of HCW at RT. The gray line shows the relative transmittance of two divided spectra taken of the same probe at different points in time.

The gray 100 % line is calculated by taking spectra of the currently studied probe at identical measurement conditions but different times and then dividing said spectra by each other. For a noise free detector and perfectly stable conditions we would expect a relative transmission of exactly 100 %. As such, the noise present in the 100 % line is an indicator of the noise in each individual spectrum and any structures visible are in essence a measurement of the setup stability. By doing this measurement we can quantify changes in temperature, pressure and atmospheric conditions both inside the FTIR spectrometer and the UHV chamber.

The most visible feature in Figure 2.7 is the broad plasmonic absorption which stretches from wavenumbers below to measurement range up to approximately 4000 cm⁻¹. Earlier research showed that this common feature for atomic metal chains can not be caused by interband transitions [19] or a phonon vibrations [20]. Furthermore, measurements of the band structure of the Au/Si surfaces show the metallicity of this surface [4]. The absorption therefore is attributed to the excitation of localized surface plasmons by IR light [5].

2.2.3 Plasmonic Excitation of Nanowires

As the length of each Au chain is finite, the plasmons form a standing wave which allows the detection by IRS through absorption. The absorption cross section $\sigma_{abs}(\omega)$ for an individual atomic chain and neglected radiation damping is modeled by a damped Lorentz oscillator

$$\sigma_{\rm abs}(\omega) = \frac{\omega_{\rm p}^2 \cdot R \cdot V}{c \cdot n_{\rm host}} \frac{\omega^2 \omega_{\tau}}{\left(x^2 - \omega^2\right)^2 + \omega^2 \omega_{\tau}^2},\tag{2.1}$$

with resonance frequency x [5]. ω_{τ} is the electron scattering rate of the electrons near the Fermi edge. The gold chain volume V is estimated from the structure models of section 2.1 and experimental data. R is the local dipole field ratio, c the speed of light and n_{host} the refractive index of the surrounding material. The plasma frequency ω_{p} is a parameter from the Drude-Sommerfeld model [21]

$$\omega_{\rm p} = \sqrt{\frac{n_{\rm e} \cdot e^2}{\epsilon_0 \cdot m^*}},\tag{2.2}$$

where n_e is the electron density, *e* the electron charge, ϵ_0 the vacuum permittivity and m^* the effective electron mass.

The local field ratio *R* is approximately 1 for very long needles, like the Au chains, and parallel polarized light. Using the thin film approximation $(1.5 \text{ Å} \approx d_{Au} \ll d_{Si} \approx 380 \,\mu\text{m})$ n_{host} can be replaced with the effective refractive index n_{eff} for a thin sheet between vacuum and Si [22]

$$n_{\rm eff} = \sqrt{\frac{1}{2} \left(1 + n_{\rm Si}^2 \right)},$$
 (2.3)

where n_{Si} is the refractive index of Si. Considering this, we find for the absorption cross section

$$\sigma_{\rm abs}\left(\omega\right) = \frac{\omega_{\rm p}^2 \cdot V}{c \cdot n_{\rm eff}} \frac{\omega^2 \omega_{\tau}}{\left(x^2 - \omega^2\right)^2 + \omega^2 \omega_{\tau}^2} \,. \tag{2.4}$$

The resonance frequency x of each individual chain linearly depends on the inverse chain length [5], which is mainly limited through naturally occurring point defects [23] as well as domain boundaries [24]. Since both of these surface defects are randomly distributed, the resonance frequencies are as well. This effect is modeled by a Gaussian broadening with mean value ω_{res} and variance $\Delta \omega$

$$G(x) = \frac{1}{\sqrt{2\pi}\Delta\omega} \exp\left[\frac{-(x-\omega_{\rm res})^2}{2(\Delta\omega)^2}\right].$$
 (2.5)

The Gaussian's mean value ω_{res} is the resonance frequency of the entire nanowire ensemble. Since we know neither ω_{res} nor $\Delta \omega$ at the outset, we have to build a fit function able to describe the measured data. To make the step from individual wires to an ensemble, we introduce the mean absorption cross section

$$\bar{\sigma}_{abs}(\omega) = \int_{-\infty}^{\infty} G(x) \,\sigma_{abs} \,\mathrm{d}x \tag{2.6}$$

$$= \frac{\omega_{\rm p}^2 \cdot \bar{V}}{c \cdot n_{\rm eff}} \frac{1}{\sqrt{2\pi}\Delta\omega} \int_{-\infty}^{\infty} \exp\left[\frac{-(x-\omega_{\rm res})^2}{2(\Delta\omega)^2}\right] \frac{\omega^2 \omega_{\tau}}{(x^2-\omega^2)^2 + \omega^2 \omega_{\tau}^2} \,\mathrm{d}x\,,\qquad(2.7)$$

which is the convolution of Gaussian and absorption cross section of the individual wire. In this step we also replaced V with \bar{V} , the average chain volume.

Since the mean absorption cross section $\bar{\sigma}_{abs}(\omega)$ contains all relevant absorption contributions and the light scattering from the nanowire sheet can be neglected due to its monolayer thickness [25], the extinction $E(\omega)$ of the nanowires is given by

$$E(\omega) = \frac{N}{A}\bar{\sigma}_{abs}(\omega) , \qquad (2.8)$$

where N/A is the number of Au chains per area which is calculated using the structure models.

The measurable quantity $T_{rel}(\omega)$, relative transmission, is related to the extinction $E(\omega)$ by the thin film approximation. One finds [22]

$$T_{\rm rel}(\omega) \coloneqq \frac{T_{\rm Si+Au}(\omega)}{T_{\rm Si}(\omega)} \approx 1 - \frac{2E(\omega) \cdot n_{\rm eff}}{(1+n_{\rm Si})}.$$
(2.9)

Inserting equation 2.7 and 2.8 in equation 2.9 we get

$$T_{\rm rel}(\omega) = 1 - \frac{2}{1 + n_{\rm Si}} \frac{N}{A} C \frac{1}{\Delta \omega} \int_{-\infty}^{\infty} \exp\left[\frac{-(x - \omega_{\rm res})^2}{2(\Delta \omega)^2}\right] \frac{\omega^2 \omega_{\tau}}{(x^2 - \omega^2)^2 + \omega^2 \omega_{\tau}^2} \,\mathrm{d}x, \quad (2.10)$$

where we introduced the fit parameter

$$C = \frac{\omega_{\rm p}^2 \cdot \bar{V}}{c\sqrt{2\pi}} \,. \tag{2.11}$$

Notably, is it very convenient that equation 2.10 does neither contain n_{eff} nor any kind of background polarizability. This is an advantage of IRS over many other measurement methods, for example electron energy loss spectroscopy, where those factors are another aspect to be considered [26].

For the spectral analysis, in order to account for baseline shifts in relative transmittance by detector and temperature drifts and additional shifts that cannot be explained as such, a frequency-independent factor b is used. As final result and fit function for the relative transmission of Au chains on Si we get

$$T_{\rm rel}\left(\omega\right) = \left(1 - \frac{2}{1 + n_{\rm Si}} \frac{N}{A} C \frac{1}{\Delta\omega} \int_{-\infty}^{\infty} \exp\left[\frac{-\left(x - \omega_{\rm res}\right)^2}{2\left(\Delta\omega\right)^2}\right] \frac{\omega^2 \omega_{\tau}}{\left(x^2 - \omega^2\right)^2 + \omega^2 \omega_{\tau}^2} \,\mathrm{d}x\right) \cdot b \,.$$

$$(2.12)$$

The applied fit function is shown in Figure 2.8.

While the plasmonic width $\Delta \omega$ and position ω_{res} and electron scattering rate ω_{τ} can be read directly from the fit result, other parameters require further assumptions and calculations to determine. Especially the average wire length \bar{L} and ratio of Fermi wave vector $k_{\rm F}$ over effective electron mass m^* are of particular interest.

2.2.4 Determination of the average Chain Length

 \overline{L} can in theory be calculated through the chain density N/A

$$\frac{N}{A} = \frac{1}{\bar{A}} = \frac{1}{\bar{L} \cdot d},\tag{2.13}$$

using the average chain area \bar{A} and the distance d of two neighboring Au chains. One has to consider though, that the fit parameter C is relatively complex. It contains not only many of the chains' electronic properties through the plasma frequency ω_p but also their geometry through their mean volume \bar{V} . Specifically the latter one can be a problem, as it results in the codependency of \bar{L} and C. Yet, one can calculate \bar{L} by adding additional information in the form of the Au chain dispersion relations.

First one sets \overline{L} to an arbitrary constant and fits the plasmonic resonance. The resulting values for *C* and \overline{L} are wrong, but their quotient is correct and the resonance position ω_{res} has been determined through the otherwise functioning fit. Through this, we can calculate the corresponding resonance energy

$$E_{\rm res} = hc \cdot \omega_{\rm res} [\rm cm^{-1}]. \qquad (2.14)$$



Figure 2.8: Example of a typical relative normal transmittance IRS spectra. The red line is the spectrum of HCW at RT. The gray line shows the relative transmittance of two divided spectra taken of the same probe at different points in time. The black line represents the applied fit discussed in this section.

which can than be inserted in the Au chain dispersion relation (Figure 2.9) to get the plasmon wave vector $k_{||}$.

Afterwards, the chain length follows through

$$\bar{L} = \frac{\pi}{k_{||}},\tag{2.15}$$

since the plasmonic resonance is the fundamental oscillation of a standing wave inside the wire [28]. Now that the real average chain length is known, one can calculate N/A and run the fit again to find the proper value for *C*.

2.2.5 Determination of $k_{\rm F}/m^*$

The calculation of the ratio of Fermi wave vector k_F over effective electron mass m^* is possible without assuming a width and a height of the chains. To do so, we use the approximation of a one dimensional chain for the electron density where the 1D electron density n_e is expressed



Figure 2.9: Plasmonic dispersion relations measured with electron energy loss spectroscopy (EELS) at room temperature. (a) Dispersion relation of Au/Si(111)- 5×2 determined from the the peak position in the EELS spectra. Solid and broken curves are theoretical calculations based on a single isolated wire with degenerate one-dimensional band and a quasi one-dimensional multi-wire model, respectively. Modified from [14]. (b) HCWs and LCWs dispersions. The solid lines denote fits assuming a quasi-1D multi wire system. Modified from [27].

by the 1D Thomas–Fermi wave vector $k_{\rm F}$ [3]

$$n_e = \frac{2k_{\rm F}}{\pi} \tag{2.16}$$

and \bar{V} is replaced by \bar{L}

$$\bar{V} \to \bar{L}$$
. (2.17)

Inserting this in the plasma frequency ω_p

$$\omega_{\rm p} = \sqrt{\frac{n_{\rm e} \cdot e^2}{\epsilon_0 \cdot m^*}} = \sqrt{\frac{e^2}{\epsilon_0 \cdot m^*} \cdot \frac{2k_{\rm F}}{\pi}}, \qquad (2.18)$$

we find for the fit factor C

$$C = \frac{\omega_{\rm p}^2 \cdot \bar{V}}{c\sqrt{2\pi}} \to \sqrt{\frac{2}{\pi^3}} \frac{e^2}{c\epsilon_0} \bar{L} \frac{k_{\rm F}}{m^*} \,. \tag{2.19}$$

and get

$$\frac{k_{\rm F}}{m^*} = \sqrt{\frac{2}{\pi^3}} \frac{ce^2}{\epsilon_0} \frac{C}{\bar{L}},\tag{2.20}$$

as end result for the Fermi wave vector k_F over effective electron mass m^* . This is a remarkable result, as it allows the calculation of band structure data from our FTIR measurements alone.

3. Setup and Experimental Work

3.1 UHV Chamber

In Figure 3.1 the most important part of our setup, the ultra high vacuum (UHV) chamber, and its components are sketched.



Figure 3.1: Schematical depiction of UHV chamber components and the beam path inside it. Modified from [29].

Using this system we can create different Silicon (Si) wafer surfaces through evaporation of Gold (Au) and C_{70} . In contrast to earlier setups, the C_{70} evaporator is a new addition. Its

construction is detailed in section 3.3. The evaporation rates can be measured through quartz crystal microbalances.

With this setup, not only the creation of new, interesting surfaces but also their measurement is possible without leaving the vacuum. The main measurement instrument is an infrared spectroscopy (IRS) using a FTIR (Fourier transform infrared) spectrometer which is directly connected to the UHV chamber via KBr windows. Apart from an optical inspection of the wafer through simple glass windows, we use an additional investigation method called RHEED (reflection high-energy electron diffraction). RHEED provides an analysis through which the surface structure, especially its periodicity, can be analyzed directly.

We can heat the probe up to $1300 \,^{\circ}$ C through resistive heating, which is needed to clean the wafer and change its structure. During the heating, the wafer temperature T is calculated from the applied current via

$$T[^{\circ}C] = 27 + 626 \cdot (I[A])^{0.26}.$$
(3.1)

This formula has been calculated from the intrinsic conductivity of doped Si and direct temperature measurements using an optical pyrometer. Notably, this relationship only holds for temperatures above $400 \,^{\circ}$ C where the Si wafers used for the experiments in this thesis become conducting [12].

Additionally a liquid helium (LHe) cryostat allows sample temperatures from room temperature (RT) down to approximately 20 K. Typical base pressures inside the chamber are around $1 \cdot 10^{-10}$ mbar.

3.2 Measurement Techniques

3.2.1 Fourier Transform Infrared Spectrometer

The most common unit throughout this thesis is the in spectroscopy widely used wavenumber notation. It refers to the inverse photon wavelength λ^{-1} [cm⁻¹] in vacuum. The wavenumber scales linearly with the photon energy

$$1 \,\mathrm{cm}^{-1} \doteq 0.124 \,\mathrm{meV},$$
 (3.2)

$$1 \text{ eV} \doteq 8065 \text{ cm}^{-1},$$
 (3.3)

making the conversion easy.

Infrared (IR) spectroscopy is a well-suited method to analyze fragile systems, like nanostructures, since it is contactless. Additionally it is relatively fast and provides an energy resolution down to 1 cm^{-1} or even lower depending on the model. Our FTIR (Tensor 27 manufactured by Bruker) produces reliable data from 500 cm^{-1} to 7000 cm^{-1} with the mercury cadmium telluride (MCT) D315 broad band detector installed. This corresponds to photon wavelengths of $20 \,\mu\text{m}$ and $1.4 \,\mu\text{m}$. Between it and the UHV chamber a polarizer is installed, enabling the polarization of the IR light.

The prevailing measurement method for all spectroscopy data presented here is the relative transmission spectra. Each such spectrum is made by dividing a sample $(T_S(\omega))$ by a reference spectrum $(T_R(\omega))$

$$T_{\rm rel}(\omega) = \frac{T_{\rm S}(\omega)}{T_{\rm R}(\omega)},$$
(3.4)

which leaves only the relative transmission differences $T_{\rm rel}(\omega)$.

Sample and reference spectra each individually consist of two more spectra, one transmission measurement through the Si wafer ($T_{S,0}(\omega)$ and $T_{R,0}(\omega)$) as well as one measurement of the empty UHV chamber ($T_{S,BG}(\omega)$ and $T_{R,BG}(\omega)$) shortly before. The latter one, the so called background measurement, is made to negate the influence of changing environmental conditions like temperature and pressure. This leaves us with

$$T_{\rm rel}(\omega) = \frac{T_{\rm S}(\omega)}{T_{\rm R}(\omega)} = \left(\frac{T_{\rm S,0}(\omega)}{T_{\rm S,BG}(\omega)}\right) \left| \left(\frac{T_{\rm R,0}(\omega)}{T_{\rm R,BG}(\omega)}\right) \right|$$
(3.5)

for each relative transmission spectrum.

3.2.2 Reflection High-Energy Electron Diffraction

Reflection High Energy Electron Diffraction (RHEED) is a commonly used method for structural analysis. The major parts of the RHEED setup, the electron gun providing a monoenergetic electron beam, a phosphorescent screen, and a clean surface are displayed in Figure 3.2. Like FTIR, RHEED has the advantage of being able to measure in situ, making it ideal for our applications. In our setup the electron beam energy is set to 20 keV and the incident angle is variable, but always below 2°. This ensures a small penetration depth of the electron beam into the studied material. Therefore, the resulting reflection patterns are only influenced by the uppermost surface layers.

Since the interpretation of RHEED images tends to be rather complicated, RHEED is commonly combined with Scanning Tunneling Microscope (STM) images or similar methods to analyze the surface directly.

3.2.3 Quartz Crystal Microbalance

A quartz crystal microbalance (QCM) is a device to measure small amounts of matter on the order of single nanograms. It operates by detecting the mass variation on its surface by



Figure 3.2: Schematic illustration of a typical of the RHEED gun analysis. The gun shoots monoenergetic electrons at the incident angle θ on the sample some of which are scattered onto the phosphorescent screen. Modified from [30].

measuring the change in frequency of a quartz crystal oscillating in resonance. It therefore is the ideal tool to adjust our evaporation rates.

The Sauerbrey equation correlates small changes of the resonant frequency Δf with small mass changes Δm of the QCM

$$\Delta f = \frac{-2f^2}{\sqrt{\rho_Q \mu_Q}} \frac{\Delta m}{A},\tag{3.6}$$

where f is the resonant frequency, A is the active electrode area, $\rho_Q = 2.65 \text{ g cm}^{-3}$ is the density and $\mu_Q = 2.95 \cdot 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$) is the shear modulus of the quartz crystal [31].

Additionally, one has to consider that QCM and sample are not at the same position. The Tooling factor TF uses simple geometric arguments to correct for the spread of the evaporation beam with increasing distance and different angles of incidence

$$TF = \left(\frac{a_{\rm S}}{a_{\rm Q}}\right)^2 \frac{1}{\cos\left(\beta_{\rm S}\right)} \,. \tag{3.7}$$

 $a_{\rm Q}$ is the distance of crucible to QCM and $a_{\rm S}$ is the distance between sample and crucible. $\beta_{\rm S}$ is the angle of incidence on the sample compared to the surface normal while the evaporation beam is assumed to hit the QCM vertically.

For the mass change per area on the sample $\Delta m_S/A_S$ we then get

$$\frac{\Delta m_{\rm S}}{A_{\rm S}} = \frac{\Delta m}{A \cdot {\rm TF}} = \frac{-\sqrt{\rho_{\rm Q}\mu_{\rm Q}}}{2f^2} \Delta f \left(\frac{a_{\rm Q}}{a_{\rm S}}\right)^2 \cos\left(\beta_{\rm S}\right) \,. \tag{3.8}$$

For thick sheets we can furthermore use the bulk density ρ of the evaporated material to calculate the sheet thickness $\Delta d_{\rm S}$ on the sample using

$$\frac{\Delta m_{\rm S}}{A_{\rm S}} = \frac{\Delta m_{\rm S}}{A_{\rm S} \cdot \Delta d_{\rm S}} \Delta d_{\rm S} = \rho \,\Delta d_{\rm S} \,. \tag{3.9}$$

For the final sheet thickness we find

$$\Delta d_{\rm S} = \frac{\Delta m_{\rm S}}{\rho A_{\rm S}} = \frac{-\sqrt{\rho_{\rm Q} \mu_{\rm Q}}}{2\rho f^2} \Delta f \left(\frac{a_{\rm Q}}{a_{\rm S}}\right)^2 \cos\left(\beta_{\rm S}\right) \,. \tag{3.10}$$

To guarantee stable conditions and a constant deposition rate, the frequency change is recorded for at least 30 minutes until a clear linear decrease of frequency per time is visible. The deposition rate is then determined by a linear fit of the temporal frequency change.

3.3 C₇₀ Evaporator

Like mentioned earlier the C_{70} evaporator is a new addition to the measurement setup. We could not use any commercially available organic evaporator, as they were all to large and hence do not fit at our chamber. Because of this we had to build our own evaporator from scratch.

To build the evaporator we solved a variety of problems. The two most significant were, that it had to be shorter than 10 cm and that it needed to heat the crucible to over 400 °C while increasing the temperature of its surroundings as little as possible. While the first problem just constrained us in the size of the jused components, the second one was made harder exactly because we constructed it ourself. This was due to the fact, that most evaporators reaching such temperatures use some kind of integrated cooling, mostly water based cooling, to minimize the temperature increase of its surrounding [32]. Considering the required effort to implemented such a system, we needed to find a less time consuming way.

First, we used the smallest crucible available (3 mm inner diameter) to minimize the material that has to be heated. Second, we thermally insulated crucible and filament with a ceramic heat shield to keep as much heat as possible at the C_{70} , where it is needed. The resulting evaporator is depicted in Figure 3.3.

The crucible and all other ceramic parts are made from aluminium oxide (Al_2O_3) as it is heat resistant, UHV suitable, isolating and relatively cheap [33]. The different colors originate from the various trace substances in the different Al_2O_3 mixtures used.

The two white ceramic plates and the ceramic pot at the bottom hold the crucible in place once it is inside the larger ceramic tube. This tube functions as heat isolation, such that we need less power to achieve the same equilibrium temperature. The crucible is heated trough resistive heating by the tungsten filament coiled around it. The filament enters the crucible through small holes in the bottom ceramic plate, wraps around the entire crucible and leaves the tube at the top, where it is brought back down through a thin isolating tube.

To measure the temperature inside the evaporator we use a thermocouple type K. Its welding point touches the inside of the ceramic tube at approximately the same height as the bottom



Figure 3.3: Pictures of our self made C_{70} evaporator. (a) The beige ceramic crucible is wrapped with a 0.2 mm diameter tungsten filament and fitted with two ceramic plates and a ceramic pot at the bottom. (b) Side picture of the entire evaporator. The crucible is inside the larger white ceramic tube. At the bottom on can see four feedthroughs coming out of the flange. The two silver colored ones, are connections to a thermocouple type K, which is inserted through the evaporator bottom. The two copper rods are used to send current through the filament, which is attached via lustre terminals to the copper. The entire evaporator from flange to its top is about 7 cm tall. (c) Birdseye view of the evaporator. The filament wire is led outside through the gap in the ceramic plate.

end of the crucible. Besides this end point, it is almost entirely enveloped in isolating ceramic, as touching the filament directly would not only distort the temperature measurement, but likely melt the thermocouple.

Using this setup, we were able to easily reach temperatures of over 500 °C while the outside of the UHV chamber directly adjacent to the evaporator was just at around 40 °C. Furthermore we successfully evaporated C_{70} at stable rates as low as 0.26 nm per minute onto our wafer.

3.4 Substrate Preparation

3.4.1 Wafer Cleaning

Before the wafer is transfered inside the UHV chamber, it is cleaned multiple times by an ultrasonic cleaner using the solvents acetone and isopropanol. After we mount the wafer in the sample holder inside the UHV transfer chamber, we pump the gas introduced by this new sample out of the chamber for two days. When the pressure sinks below $1 \cdot 10^{-8}$ mbar we transfer it to the main chamber and start the first cleaning process, the so called degassing. We slowly heat the wafer via resistive current heating to 700 °C over a period of approximately 20 hours, during which most of the residual gas desorbs from the wafer. Because this greatly increases the chamber pressure we take great care to perform the degassing as slowly as

possible, waiting with additional temperature increases until the pressure falls back to its baseline. After the degassing the wafer is almost completely free of gas and other adsorbates, nearly ready to be used in experiments. On more cleaning step is necessary though, the so called flashing.

3.4.2 Flashing

After the wafers have been freed of residual gas particles, the last obstacle preventing its use as nanowire substrate is the naturally occurring silicon dioxide forming the uppermost surface layer on all silicon that has been in contact with the atmosphere. While flashing is a common method to achieve this goal and its fundamentals are always the same, the details vary considerably throughout research [12]. In our research group, the following procedure has achieved the best results.

At first, the wafer is slowly heated to about $450 \,^{\circ}$ C to establish its conductivity necessary for resistive heating. This is done to avoid high voltage and current spikes, resulting in an uneven and unpredictable heating and possibly damaging the wafer. Following this the wafer is heated to ever higher temperatures in consecutively increasing current bursts of one to two seconds length. The pause time after each burst is dictated by the time it takes for the chamber pressure to fall back to its baseline. An example is shown in Figure 3.4



Figure 3.4: Schematic heat treatment diagram for flashing of Si samples in UHV. Between 900 °C to 1060 °C SiC is formed on the surface. Modified from [10].

Temperatures up to 1200 °C, only a little below the melting point of silicon, are reached. After the last peak, the so called annealing is performed, where the temperature is held constant at around 830 °C for a couple of minutes, before it is gradually lowered to RT. The main reason for this is the Si(111) phase transition at 830 °C which changes the silicon surface from the 1×1 to the 7×7 reconstruction. This structure is necessary for the formation of the stable, ordered steps discussed in section 2.1. The temperature is held for minutes instead of seconds, since the top three surface layers have to be reordered to construct the 7×7 surface, making the necessary mass transport enormous. Further details of this phase change, the processes involved and its effect on the Si(111) steps can be read in the PhD thesis of Chung Vu Hoang [30].

During our experiments we found, that flashing the Si(553) wafers up to $1300 \,^{\circ}$ C instead of $1200 \,^{\circ}$ C resulted in the removal of thin Silicon carbide (SiC) layers while not damaging the wafers (Figure 3.5).



Figure 3.5: Pictures of the same Si wafer after different increasing flashing temperatures (**a**) Wafer after flashing with 1200 °C. The white SiC sheet is still very pronounced in the upper left and lower right corner. (**b**) Wafer after flashing once with 1300 °C. The SiC coverage has gone back significantly. (**c**) Wafer after flashing multiple times with 1300 °C. No more SiC is visible in the lower right corner and only a small part of the upper left corner is still covered with SiC.

This white substance forms in the temperature region of 900 °C to 1060 °C from natural carbon impurities inside the Si [18]. SiC normally accumulates over multiple flashings and makes the wafer unusable after a couple of experiments. But, because of this discovery, we barely had to replace our Si(553) wafers, which greatly increased the speed at which we were able to test different setups.

In our setup, the entire above described procedure is controlled and monitored by a LabVIEW program that was devoloped during the scope of this thesis.

3.5 Controlling Program

One of the larger pieces of experimental work I did was writing a LabVIEW program, building on and unifying the already existing programs. Its main functionality is the control of the power supply used to heat and flash the wafer as well as the C_{70} evaporator through resistive heating.

3.5.1 Wafer Heating

One of the main applications is the flashing process. During this the wafer is heated to ever higher temperatures up to $1300 \,^{\circ}$ C, only a little below the melting point of silicon, in consecutively increasing current bursts of one to two seconds length. If the flashing is not done for precise time intervals and currents the damage to the wafer can be extensive. On the one hand a too high, too long applied, or too fast altered current might melt or break the wafer. On the other hand, the opposite might not sufficiently clean the wafer for further use. Because of this, even a small mistake can warrant a wafer replacement costing multiple days.

In the past, everything was controlled by hand and as such every flashing was different from the last. Today, the entire procedure is automated from start to finish. One can now set the ideal flashing procedure once and execute it with a button press. This guarantees a reproducible result, maximizes the quality of the wafer surface and eliminates human errors from the entire procedure.



Figure 3.6: Set temperatures of an automated flashing example, calculated from the applied current. (a) Overview over the entire flashing procedure. In this example, the wait time between the peaks was set constant. (b) Individual temperature burst as used in flashings. Once can clearly see the high peak symmetry.

The program can also be used in the degassing process, which has to be done every time a new wafer is transferred to the main chamber. With this, one can start and stop heating via remote

control without being in the lab, maximizing efficiency. It can even be used to heat a new wafer independently over the weekend, as is needed to remove the residual gas on its surface.

3.5.2 Heating of the C₇₀ evaporator

The second main application is controlling the C_{70} evaporator. While heating an evaporator is in principle an easy and straight forward task, this is not the case for organic materials. Inorganic materials are in general easy to evaporate, because they are inert and stable as long as they are kept in a vacuum. The only process they undergo is the desired phase change from solid to gas. For this reason, the biggest concern when evaporating inorganic materials is mostly not the material itself, but the coil or filament used to heat the evaporator, which could break from increasing the current to fast. Yet, the typical heat up process for inorganic evaporators is still relatively short. For example, the beam evaporator used in our lab to evaporate gold takes about five minutes until the maximum current is reached.

Organic materials are not nearly as stable. For example can heating or cooling of C_{70} too fast lead to crust formation on the material's surface or its decomposition to smaller carbon molecules [34]. Should this happen, the entire content inside the crucible becomes useless.

To prevent this, a temperature change of smaller than 5 °C per minute turned out to be safe [34]. Since temperatures around 400 °C are needed to evaporate C_{70} in vacuum, manually controlling the heat up and cool down phases is over an hour of work. Through testing, we found the evaporator temperature curve to be constant between experiments, making this a straight forward task to automate.

4. Au Chains on Si(553)

The main experiment of this thesis was the IR spectroscopy of HCW and LCW Au chains on Si(553), investigating a remarkable shift of the plasmon absorption maximum to lower wavenumbers at lower temperatures.

4.1 Preparation and Process

The substrates used in this experiment were Si(553) wafers (p-type doped, double side polished, 5-6 Ω cm resistivity) with an off-cut angle of 12.3° from the [111] toward the [112] direction, as explained in section 2.1.

Like in any experiment, we began by degassing and flashing the Si(553) wafers. Once they were clean, we took spectra of the pristine wafers (reference spectra) at the temperatures and polarizations we planned to measure later. Having done that, we carefully adjusted the evaporation rate via the QCM before evaporating onto samples at a deposition rate of 0.1 ML per minute.

To prepare the HCW and LCW chains on Si(553), we evaporated 0.46 ML or 0.19 ML, respectively onto the Si wafers at a sample temperature of 600 °C. The evaporation was followed by approximately 1-2 seconds of post-annealing at 800-870 °C. On some HCW samples we deposited additional 0.05 ML Au at RT after the pristine chains were formed. This structure is from here on called HCW+0.05 ML.

RHEED pictures and FTIR spectra with the Au chain covered wafers (sample spectra) were then taken at the temperatures and polarizations corresponding to the reference spectra of the pristine wafers. The relative transmittance spectra ($T_{rel}(\omega)$) shown in the next section were then calculated by dividing the sample spectra ($T_S(\omega)$) by these reference spectra ($T_R(\omega)$) via

$$T_{\rm rel}(\omega) = \frac{T_{\rm S}(\omega)}{T_R(\omega)},\tag{4.1}$$

as explained in section 3.2.1.

For all spectra (reference and sample) a resolution of 8 cm⁻¹ was used unless otherwise noted.

4.2 High Coverage Wires

To make sure that we did in fact construct the HCW surface structure proposed by Krawiec in 2010 [9] we examined the surface using RHEED. The resulting refraction pattern of a sample at 20 K are shown in Figure 4.1.



Figure 4.1: RHEED pattern of HCW at 20 K. Marked by the red, dashed lines are the 1×2 streaks. Additionally the 1×3 streaks, represented by blue, dashed lines, are visible. The green, dashed lines mark equal points of inset and original RHEED picture.

The RHEED pictures contain modified insets to highlight the streak visibility and reduce noise. The modification is explained in detail in section A.1. One of the most striking features in Figure 4.1 are the 1×2 streaks which result from the twofold periodicity of the 1×2 unit cell at RT predicted by Krawiec [9] (see Figure 2.5). The reason that we see streaks and not points as normally expected from RHEED, is that the $\times 2$ periodicity only holds inside individual chains. While the distance between two atoms along the chains is fixed, the individual atoms of neighboring chains have no fixed phase relation between them. This is because any chain can shift by a Si basis vector parallel to the chain orientation and still be in an equivalent energetically favorable position. Seeing those streaks at such high intensity, shows that we did indeed construct the HCW structure on the whole wafer.

Next, we can spot another key feature of the HCW surface, the 1×3 streaks. These streaks result from the antiferromagnetic spin ordering of the HCW surface at low temperatures predicted by Erwin et al. [16] (see section 2.1.2). Naively one would expect to see 1×6 streaks for the spin ordered HCW surface, since the unit cell triples its periodicity from 1×2 to 1×6 . For RHEED measurements however, only the crystal lattice properties resulting

in different electron refraction angles are visible. Because the electron beam send from the RHEED gun is not spin-polarized, only the height change resulting from the the ordered spin of the Si edge atoms is not visible, only the spin itself. This height change of about 0.3 Å is present in every third Si atom [16], resulting in the 1×3 streaks we see here.

In total our RHEED pattern agrees with other RHEED measurements of this structure [35]. In Figure 4.2 IR spectra of HCWs at RT and at 20 K are shown.



Figure 4.2: Relative normal transmittance spectra of HCW at different temperatures. Solid lines denote a parallel to the chains polarized IR light, while dotted lines represent orthogonal polarization. The black lines on top of the measured curves are calculated via the fit discussed in section 2.2.3. The color gradient denotes multiple measurements between 20K and RT. The dotted, black line depicts the shift of the absorption maximum to the lower wavenumbers for lower temperatures. The gray 100% line is made by measuring twice at the same conditions and then dividing both spectra by each other. It is thereby a measure of the setup stability. [36].

As typical for the transmission spectra of atomic Au chains on Si, one can see the broad absorption of localized surface plasmons, the resonance of which corresponds to the absorption maximum. Starting with the HCWs at RT, the total absorption at the plasmon resonance is approximately 4%. The signal at 20 K gets sharper and increases to 6%. The absorption at 20 K also shifts to lower wavenumbers compared to the resonance at RT.

Furthermore, the spectra of the $[11\overline{2}]$ (orthogonal to the chains) polarized light, shows no

plasmonic resonance, indicating a very strong chain growth preference towards the [110] direction. This strong chain growth anisotropy is another indicator of a well reconstructed HCW surface.

The temperature gradient contains one measurement every 20 K during the four hour warm up of the sample after cooling. One can see that the absorption signal progressively gets broader, weaker and shifts to higher wavenumbers again. Once at RT, it coincides with the original RT spectrum again, implying that the process is reversible and the surface structure was unaffected by the cooling. The temperature change of less than 3 K during each individual measurement was insignificant for the overall trend.

Using the fit at RT and 20 K we found that the electron scattering rate decreases from

$$\omega_{\tau,\text{RT}} = 1275 \,\text{cm}^{-1} \text{ to } \omega_{\tau,20\,\text{K}} = 1079 \,\text{cm}^{-1},$$
(4.2)

with a relative error of 10%. This electron scattering rate decrease was expected, as it has been observed before on many different surfaces [37]. The explanation is a reduction in electron-phonon scattering at lower temperatures, which in turn is the result of a decrease in the amount of excited phonons at lower temperatures [5].

For the Fermi wave vector $(k_{\rm F})$ over effective electron mass (m^*) we get

$$\frac{k_{\rm F}}{m^*}\Big|_{\rm RT} = (1.37 \pm 0.3) \,({\rm \AA m_e})^{-1} \text{ and } \frac{k_{\rm F}}{m^*}\Big|_{20\,\rm K} = (1.67 \pm 0.3) \,({\rm \AA m_e})^{-1} \,. \tag{4.3}$$

where m_e is the free electron mass.

During cooling, the resonance frequency shifts from

$$\omega_{\text{res,RT}} = (1045 \pm 5) \text{ cm}^{-1} \text{ to } \omega_{\text{res,20 K}} = (905 \pm 9) \text{ cm}^{-1},$$
 (4.4)

for a total difference of

$$\omega_{\text{res,shift}} = (-140 \pm 10) \,\text{cm}^{-1}$$
 (4.5)

This shift of the plasmon resonance to lower wavenumbers is very intriguing as it stands in disparity to recent measurements of the Au/Si(111)-5 \times 2 system. There, a shift of the absorption maximum to higher wavenumbers due to less electron-phonon scattering was found [5]. The shift to higher wavenumbers is also what one would expect from a naive application of plasmon and condensed matter theory, precisely because of the reduction in the number of phonons at lower temperature.

4.3 Doping HCWs with additional Gold

To research this phenomenon further, we used the findings of Song et al. in 2014 [38]. He and his colleges showed that it was possible to control the three metallic Au bands of the



Figure 4.3: Influence of Au doping on the HCW's electronic structure. (**a**) Change of the electronic bands from HCWs (pristine) to HCWs+0.05 ML (Au 0.048 ML). The S_2 band shifts to a higher binding energy, but roughly maintains its intensity near the Fermi edge (Binding energy of 0 eV). S_1 and S'_1 keep their shape, but loose a considerable amount of intensity near the Fermi edge. Modified from [38]. (**b**) Momentum Distribution Curves (MDCs) of ARPES intensity maps at E_F . While S_2 stays largely unaffected by Au amounts below 0.048 ML, only shifting to higher Fermi wave vectors with increased doping, the S_1 and S'_1 bands continuously loose intensity until they are barely measurable at 0.048 ML. Modified from [38].

HCW surface by depositing additional Au atoms on the already formed HCWs. Some of their results are shown in Figure 4.3.

Using angle-resolved photo emission spectroscopy (ARPES) they showed the added electrons are localized only in one of the three bands, the S_2 band. S_2 is simultaneously the only band with non-vanishing intensity at the Fermi energy E_F after additional 0.048 ML Au have been evaporated onto the pristine HCWs. As a result, it is the only metallic band left on the HCW+0.05 ML surface, since the other two, the S'₁ and S₁ bands, have become isolating.

We constructed the HCWs+0.05 ML to examine the effects of the absence of the S'₁ and S₁ bands might have. We again verified our sample with RHEED measurements depicted in Figure 4.4.



Figure 4.4: RHEED pattern of HCW+0.05 ML at 20 K. Marked by the red, dashed lines are the 1×2 streaks, while the 1×3 streaks are again marked by blue dashed lines. The green, dashed lines represent equal points of inset and original RHEED picture.

First and foremost, the HCW+0.05 ML RHEED and the HCW RHEED patterns show the same refraction patterns of 1×2 and 1×3 streaks. Because of this, we can be infer that the additional 0.05 ML Au did not change its periodicity to such a degree that it is no more comparable to the old surface. Compared to the HCWs, the 1×2 streaks are here easily visible as well, even though they did loose a lot of sharpness and intensity. Although the 1×3 streaks of the HCWs+0.05 ML are barely visible, the lost intensity is much less compared to the 1×2 streaks, since they were faint even in the very well reconstructed HCWs of Figure 4.1.

Considering that the antiferromagnetic spin order of the Si step edge is a fragile phenomenon [16] it is astounding that we can still see its effect after the surface has been considerably disturbed by the dopant. However weak the 1×3 streaks might be, still being able to see them at all with RHEED is remarkable, although not entirely unexpected. Song predicted via surface free-energy calculations that the extra Au atoms prefer to adsorb near the Au nanowires and not near the step edges [38]. If the Au atoms adsorb near the Au chains, their order should decrease and with it the intensity of the 1×2 streaks. Meanwhile the 1×3 streaks should loose less signal since Au atoms adsorb near the step edges and disturb the antiferromagnetic ground state. This is exactly the influence we were able to confirm with our RHEED pictures.

In total, our findings strengthen the theory of Song et al. in that the 0.05 ML additional Au atoms is too small to seriously damage the unit cell structure and more Au atoms adsorbed

near the Au wires instead of the step edges.

Continuing with the IR spectra of HCWs and HCWs+0.05 ML, shown in Figure 4.5, it is noticeable that the HCWs+0.05 ML absorption is with about 2% much lower than the absorption of the HCWs both at RT and at 20 K.



Figure 4.5: Relative normal transmittance spectra of HCWs+0.05 ML (solid lines) and pristine HCWs (dashed lines). The red curves were taken at RT, the blue curves at 20 K. The black lines on top of the measured curves are calculated via the fit discussed in section 2.2.3 The gray 100% line is made by measuring twice at the same conditions and then dividing both spectra by each other.

This decrease in the plasmonic signal is probably the result of less free charge carriers contributing to the absorption. This in turn is caused by the intensity loss of the S_1 and S'_1 bands at the Fermi edge. As such, the diminished absorption relative the HCWs is a clear sign of a changed electronic band structure. Additionally, Song et al. calculated that this intensity loss of the S_1 and S'_1 bands only occurs if most additional Au atoms adsorb near the chains and not the step edges. [38] Since we clearly see the effect of these isolating bands in the decreased plasmonic resonance, this is another indication, that his theory of the Au atoms adsorbing primarily near the chains is correct.

Importantly, the HCW spectra shown in Figure 4.5 are from the same sample used to

prepare the HCWs+0.05 ML shown, with no annealing in between, ensuring identical chain length of HCWs and HCWs+0.05 ML. Since the Au chain length, and because of that the resonance frequency, heavily depend on wafer preparation and heat treating, this allows the comparison of quantities normally varying between samples, like absolute resonance frequencies. Furthermore, we can use the HCWs to calculate the chain length of both systems. This allows the determination of quantities like the ratio of Fermi wave vector k_F to effective electron mass m^* even though the dispersion relation of the HCWs+0.05 ML is currently unknown.

Comparing HCW and HCW+0.05 ML absorptions at equal temperatures, it is noticeable that the plasmonic resonance of the HCW+0.05 ML lies at a higher wavenumber than the HCW one. Song et al. showed that the additional Au does not cause local disorder but merely acts as an electron dopant until a critical doping level of 0.048 ML was reached [38]. Since we did not significantly exceed this limit, the effective chain length should not have decreased between HCW and HCW+0.05 ML. This again stands in contrast with the Au/Si(111)-5 × 2 surface where, similar to naturally occurring defects and adatoms, the Au dopants induce additional local disorder, decreasing the average chain length [5]. The reason why the HCW+0.05 ML resonances lie at higher wavenumbers than the corresponding HCW ones must then be a different dispersion relation of the HCWs+0.05 ML, likely resulting from the missing contribution of the two bands S'₁ and S₁.

While the HCW+0.05 ML absorption maximum gets sharper and stronger at low temperatures, the effect is considerably less than for the HCWs. Using the fit, we can again determine the electron scattering rates ω_{τ} and resonance frequencies ω_{res} . We find

$$\omega_{\tau,\text{RT}} = 1640 \,\text{cm}^{-1} \text{ to } \omega_{\tau,20\,\text{K}} = 1212 \,\text{cm}^{-1},$$
(4.6)

(with a relative error of 10%) for the electron scattering rates. As with the HCWs, the increased absorption sharpness at lower temperatures is likely explained by less electron-phonon coupling.

For Fermi wave vector $(k_{\rm F})$ over effective electron mass (m^*) we find

$$\frac{k_{\rm F}}{m^*}\Big|_{\rm RT} = (0.90 \pm 0.3) \,({\rm \AA m_e})^{-1} \text{ and } \frac{k_{\rm F}}{m^*}\Big|_{20\,\rm K} = (0.74 \pm 0.2) \,({\rm \AA m_e})^{-1} \,. \tag{4.7}$$

We can compare them to the HCW surface for which we got $k_F/m^*|_{RT} = (1.37\pm0.3) (\text{Åm}_e)^{-1}$, $k_F/m^*|_{20 \text{ K}} = (1.67\pm0.3) (\text{Åm}_e)^{-1}$. One can clearly see that the values of the HCWs+0.05 ML are smaller compared the the HCWs, which is likely caused by the missing contribution of the two bands S'₁ and S₁ resulting in a smaller effective k_F . Notably, m^* is also different between the systems, which we can estimate using ARPES data of S₂ by Song et al. [38]. We find

$$m^* = 0.29 \,\mathrm{m_e} \quad (\mathrm{HCW}),$$
 (4.8)

$$m^* = 0.39 \,\mathrm{m_e} \quad (\mathrm{HCW} + 0.05 \,\mathrm{ML}) \,.$$
 (4.9)

which we can use to estimate the $k_{\rm F}$

$$k_{\rm F}|_{\rm RT} \approx 0.40 \,\text{\AA}^{-1} , \ k_{\rm F}|_{20 \,\rm K} \approx 0.48 \,\text{\AA}^{-1} \quad (\rm HCW),$$

$$(4.10)$$

$$k_{\rm F}|_{\rm RT} \approx 0.35 \,\text{\AA}^{-1} , \ k_{\rm F}|_{20 \,\rm K} \approx 0.29 \,\text{\AA}^{-1} \quad (\rm HCW+0.05 \,\rm ML),$$
 (4.11)

where the same trend still holds.

The resonance frequencies shift from

$$\omega_{\text{res,RT}} = (1015 \pm 3) \text{ cm}^{-1} \text{ to } \omega_{\text{res,20 K}} = (949 \pm 2) \text{ cm}^{-1},$$
 (4.12)

for a total difference of

$$\omega_{\text{res,shift}} = (-66 \pm 5) \,\text{cm}^{-1},$$
 (4.13)

which is smaller by a factor of about 2 relative to the HCWs.

Curious that the shift is still present, even tough two of three metallic bands do not contribute to the plasmonic excitation anymore, we theorized that the underlying unit cell, especially the unique spin ordered ground state, might be fundamental for this phenomenon. Wanting to test this hypothesis, we prepared LCWs.

4.4 Low Coverage Wires

In Figure 4.6 the energy distribution curves and electronic band structures of LCWs and HCWs are shown.

Comparing both band structures, they both have three similar bands at roughly the same momenta with a non-vanishing intensity near the Fermi edge (here depicted as a binding energy of 0 eV). Song et al. predicted S_1 , S'_1 and S_2 to be metallic and behave very similar to the HCWs, even though relative to the HCWs only 39% of Au is deposited of the surface [1]. Classically, this would have not been expected, since most other atomic nanowire systems are very sensitive to the amount of gold deposited and even small amounts of missing material, on the order of 10%, can destroy the metallicity of the surface completely, as no chains are able to form [12]. Knowing the unit cell structure though, this is no surprise as these bands result mostly from the gold chains which are structurally almost identical in both systems. This is explained by the lower chain density in the LCW system, where every second Au chain is replaced by the Si 5×5 honeycomb strip (see section 2.1.3).

This additional Si 5×5 strip is also has the benefit of putting strain on the Au chain covered steps, deforming the step edges slightly such that no antiferromagnetic order at low temperatures can form. Due to this strain, we can test if the antiferromagnetic order is a major factor in the plasmonic resonance shift. It is furthermore likely to be the cause of the S₃ band



Figure 4.6: Energy distribution curves (momentum= 0.85 Å^{-1} , left) and electronic band structures (right) of LCWs and HCWs measured by ARPES with a photon energy of 46 eV. In both LCWs and HCWs three bands S₁, S'₁ and S₂ with a non-vanishing intensity at the Fermi edge are present. Unique to the LCWs is an additional S₃ band (blue) and a reduced intensity region (arrow) on the S₁, S'₁ bands. Modified from [1].

only present in the LCWs, but since this band has no intensity near the Fermi edge, we should not be able to excite it with IR light and due to that not see it in the FTIR spectra.

We again verified our sample with RHEED measurements depicted in Figure 4.7.



Figure 4.7: RHEED pattern of LCW at 20K. The two insets show the RHEED picture at RT and 20K. The red, dashed lines denote 1×2 streaks, the blue, dashed lines 1×5 streaks. The green, dashed lines mark equal points of insets and original RHEED picture.

Again, we find the 1×2 streaks as a major feature of the refraction pattern. Here too, they are the result of the twofold periodicity of the gold chains. As expected, no 1×3 streaks are present, since the LCWs do not have a spin ordered ground state like the HCWs. However, 1×5 streaks are visible. This new characteristic is generated by the 5×5 Si strip between every step occupied by Au chains. In total, the RHEED pattern agrees with the unit cell proposed by Song et al. [1].

Examining the FTIR spectra in Figure 4.8, we can easily identify the familiar plasmonic resonance, proofing that the LCWs are indeed metallic. The much lower absorption maxima



Figure 4.8: Relative normal transmittance spectra of LCW at different temperatures. Solid lines denote a parallel to the chains polarized IR light, while dotted lines represent orthogonal polarization. The black lines on top of the measured curves are calculated via the fit discussed in section 2.2.3. The gray, dotted 100% line is made by measuring the same sample at the same conditions and dividing both spectra by each other.

of around 1.5% and 2% at RT (red) and 20 K (blue) compared to the HCWs is explainable due to the lower chain density per area. For polarization orthogonal to the atomic chains ([11 $\overline{2}$]) no plasmonic absorption can be observed, signifying a very anisotropic chain growth, very similar to the HCWs.

Quantitatively, we calculate electron scattering rates of

$$\omega_{\tau,\text{RT}} = 1622 \,\text{cm}^{-1} \text{ and } \omega_{\tau,20\,\text{K}} = 1315 \,\text{cm}^{-1},$$
 (4.14)

(with a relative error of 10%), which explains the stronger and sharper plasmonic resonance at 20 K with less electron-phonon scattering, here too.

The resonance frequency shifts from

$$\omega_{\text{res,RT}} = (850 \pm 3) \,\text{cm}^{-1} \text{ to } \omega_{\text{res,20 K}} = (740 \pm 1) \,\text{cm}^{-1},$$
 (4.15)

for a total difference of

$$\omega_{\rm res, shift} = (-110 \pm 3) \,\rm cm^{-1}, \qquad (4.16)$$

which is much closer to the $\omega_{\text{res,shift}} = (-140 \pm 3) \text{ cm}^{-1}$ from the HCWs than it is to the $\omega_{\text{res,shift}} = (-66 \pm 3) \text{ cm}^{-1}$ shift of the HCWs+0.05 ML.

The LCWs therefore really behave analogously to the HCWs, agreeing with the predictions of Song et al.

4.5 Summary

In this experiment we prepared and examined three different kinds of surfaces, the HCWs, HCWs+0.05 ML, and LCWs via RHEED and FTIR spectroscopy. All our RHEED patterns agree with the prevailing structural models and measurements [35], [9], [16], [38], [1] for all three types of wires.

Our findings strengthen the theory of two papers by Song et al. [38], [1] in that 0.05 ML additional Au atoms is a too small amount of dopant to seriously damage the HCW unit cell structure and more of these extra Au atoms adsorb near the Au wires instead of the step edges [38]. Additionally we could confirm that the intensity of the S_1 and S'_1 bands at the Fermi edge vanishes for this amount of Au dopant. The LCWs RHEED pattern, and their IR absorption indicate that Song et al. predicted unit cell is correct, that they are indeed metallic and behave similar to the HCWs [1].

Like in many nanowire systems, all the plasmonic resonances became sharper and stronger at lower temperatures, which we explain via less electron-phonon scattering. We calculated scattering rates of

$$\omega_{\tau,\text{RT}} = 1275 \,\text{cm}^{-1} , \, \omega_{\tau,20\,\text{K}} = 1079 \,\text{cm}^{-1} \quad (\text{HCW}),$$
(4.17)

$$\omega_{\tau,\text{RT}} = 1640 \,\text{cm}^{-1}$$
, $\omega_{\tau,20\,\text{K}} = 1212 \,\text{cm}^{-1}$ (HCW+0.05 ML), (4.18)

$$\omega_{\tau,\text{RT}} = 1622 \,\text{cm}^{-1}$$
, $\omega_{\tau,20\,\text{K}} = 1315 \,\text{cm}^{-1}$ (LCW). (4.19)

For all three systems, the plasmonic resonance absorption maximum shifts to lower wavenumbers for lower temperatures:

$$\omega_{\text{res,shift}} = (-140 \pm 10) \,\text{cm}^{-1}$$
 (HCW), (4.20)

$$\omega_{\text{res,shift}} = (-66 \pm 5) \,\text{cm}^{-1} \qquad (\text{HCW}+0.05 \,\text{ML}),$$
 (4.21)

$$\omega_{\text{res,shift}} = (-110 \pm 3) \,\text{cm}^{-1}$$
 (LCW), (4.22)

This stands in contrast with recently measured shifts of the Au/Si(111)-5 \times 2 to higher wavenumbers at lower temperatures due to less electron-phonon scattering [5] and naive application of plasmon and condensed matter theory [21].

A simple measurement error cannot be responsible for this behavior, since the shift could be reproduced for multiple samples of the same type and was observed for the three different surface structures HCW, HCW+0.05 ML and LCW. Furthermore we could exclude the antiferromagnetic ground state of HCW and HCWs+0.05 ML as a major factor in this shift, since we observed it for the LCW surface as well.

We managed to create HCWs and HCWs+0.05 ML such that a three fold periodicity in the RHEED measurements at 20 K appeared which is currently best explained by their presumably antiferromagnetic ground state. Since we furthermore examined the LCWs for which this state was not predicted, and no sign was found in our RHEED patterns, but the shift was still present, we can exclude the HCW's antiferromagnetic ground state as single cause behind this phenomenon.

One possible explanation is a reversible reordering of the Au atoms at lower temperatures, which could result in a slightly different dispersion relation. If this reordering only happens for these exact Au wire configurations, it would explain that this shift is only present for the HCWs, HCWs+0.05 ML and LCWs which are the only known surfaces with this Au wire configuration.

5. C₇₀ doping of Au chains on Si(111)

The second big experiment carried out was the doping of Au chains on Si(111) with C_{70} and additional Au, examining a possible electron transfer.

5.1 C₇₀ Doping Motivation

 C_{70} belongs to the family of fullerenes. Figure 5.1 depicts its cage like structure, resembling a rugby ball. It is made up of 70 carbon atoms and very stable under pressure and temperature changes. Furthermore C_{70} is chemically inert and should not react with the Au chains or the Si surface at RT once brought into contact.

Doping the Au chains with C_{70} has the goal of transferring electrons from the chains to the C_{70} molecules. If this succeeds, the half filled electron bands of the Au chains are emptied, decreasing their conduction and in turn influencing the behavior under IR light and the plasmonic resonance we see in the FTIR spectra.

For electrons to leave their orbital, they normally have to be



Figure 5.1: 3D representation of the C_{70} structure [39].

excited with such high energies, that they leave the material altogether (for example in the photoelectric effect) or they have to be brought in close contact with a material that has free orbitals of lower energies such that it is energetically favorable for the electrons to transfer into that new orbital.

The lowest unoccupied molecular orbital (LUMO) of C_{70} lies at $E_{LU} = 4.6 \text{ eV}$ [40], while the Au chain Fermi energy is about $E_F = 4.8 \text{ eV}^{-1}$ [41] relative to the vacuum level. This results in a first energy gap approximation of 0.2 eV. Importantly, this energy is not accurate for our purposes, since the 0.2 eV neglect interaction of C_{70} and sample as well as several energy

¹ The Fermi energy of the Au/Si(111)-5 \times 2 unit cell has been calculated by solving the electrostatic potential at the surface and determining the work function. An experimentally measured value would likely be slightly higher since the calculation has been done without taking quasi particle effects into account [41].

broadaning effects [42].

First and foremost, the LUMO bandwidth of C_{70} resulting from intermolecular interactions is found to be as high as 0.5 eV [43]. While this effect is certainly weaker for the first layers of C_{70} on our substrate, it is not negligible and should only increase in magnitude if more C_{70} is deposited on the surface. Furthermore a shift of the LUMO band to higher energies is expected to occur through the polarization background of the Au/Si surface. This can be roughly estimated in analogy to doped crystal semiconductors, for example Si doped with arsenic (As). In this system, the tetravalent Si atoms force the pentavalent As into a bond with four neighboring Si atoms, leaving one As electron unbonded. At low temperatures, the electron donor system behaves similar to a hydrogen system with energy eigenstates

$$E_n = -\frac{1}{2} \frac{m^* e^4}{(4\pi\epsilon_r\epsilon_0\hbar)^2} \cdot \frac{1}{n^2},\tag{5.1}$$

with principal quantum number *n*, electron charge *e*, effective electron mass m^* , vacuum permittivity ϵ_0 and permittivity of the surrounding material ϵ_r . In comparison with classical hydrogen this system's energy eigenstates are lowered twofold. Besides the (typically) smaller mass term m^* , the relevant factor for our C₇₀ experiment is the permittivity of the surrounding material ϵ_r which is always greater than one [44].

Combining the influence of these effects, we expect electrons to transfer from the Au chains to the C_{70} . The magnitude of this transfer is the measurement goal of the following experiments. While 1 ML still represents one atom or molecule per Si(111)-1 × 1 unit cell, we define another notation here. The ML_{5×2} stands for one atom or molecule per 5 × 2 unit cell. Since the 5 × 2 cell has per definition ten times the area of the 1 × 1 cell the obvious relation

$$10 \,\mathrm{ML}_{5 \times 2} = 1 \,\mathrm{ML},$$
 (5.2)

holds. We use it here to denote the amount of C_{70} for a two main reasons.

First and foremost, the width of C_{70} is on the order of 1 nm [45] which is actually much wider than the approximately 3 Å width of a Si(111)-1 × 1 unit cell [4]. Considering this, a 1 ML coverage of C_{70} is already several layers thick, which makes it unwieldy as a measure of surface coverage and the notation of "monolayer" rather misleading.

Conveniently, the cross section of $C_{70} A_{C_{70}} = (1.25 \pm 1.8) \text{ nm}^2$ (calculated by squaring the maximum diameter of C_{70} from [45]) is about the area of a 5×2 unit cell $A_{5\times2} = 1.23 \text{ nm}^2$ [4], meaning that $1 \text{ ML}_{5\times2} C_{70}$ is approximately the maximal C_{70} coverage where every C_{70} molecule is able to touch the surface.

Second, previous work found that one free electron per Au/Si(111)-5 × 2 cell contributes to the plasmononic absorption [5]. For a C_{70} coverage of $1 ML_{5 \times 2}$ there is one C_{70} molecule touching the surface and one free electron in the Au chains. As such, $ML_{5 \times 2}$ notation signifies the relative amount of C_{70} molecules to free surface electrons.

The nm thickness we additionally use to specify the C_{70} amount in a more intuitive way has been calculated (as explained in section 3.2.3) via the C_{70} bulk density $\rho = 1.7 \text{ g/cm}^3$, which we estimated to be accurate for three or more layers of C_{70} . Using this density, 1 nm C_{70} corresponds to 3.11 ML_{5 × 2}, roughly 3 layers, of C_{70} . As such we use nm to denote the thickness of C_{70} layers greater than 3 ML_{5 × 2}.

All the evaporation amounts specified for C_{70} in this chapter indicate the amount of substance that was evaporated onto the sample as calculated via QCM measurements and tooling factor (see section 3.2.3). This is important as we estimate that the amount of C_{70} sticking to the sample is 20% lower than the one evaporated, which was measured through preliminary Atomic-force microscopy (AFM) and ellipsometry measurements.

For the deposition of Au, the QCM predicted rates are accurate. This was checked by comparing the theoretically needed 0.7 ML Au for the ideal Au/Si(111)-5 × 2 surface with RHEED pictures of the experimentally manufactured structure. The Au coverage with maximal signal strength and sharpness of the characterizing 5×2 RHEED pattern and no visible patterns from the underlying Si(111)-7 × 7 substrate corresponded very well with the 0.7 ML Au predicted [12]. Additionally, the Au coverage error is not significant as RHEED measurements clearly show how well reconstructed the chains are.

5.2 Preparation and Process

In this experiment Si(111) wafers (p-type doped, double side polished, 5-6 Ω cm resistivity) with an intentional off-cut of 1° toward [112] as explained in section 2.1 were used as substrate. As before, we began by degassing and flashing the Si(111) wafers and then took the reference spectra of the pristine wafers.

The Au evaporation rate was adjusted to 0.1 ML Au per minute via the QCM. For C_{70} varying rates were used which are stated in the following sections. To construct the Au chains on Si(111) a total of 0.7 ML were evaporated onto the wafers at a sample temperature of 600 °C which were then post-annealed for approximately 2 seconds at 800 °C afterwards.

We took RHEED pictures after every major step to control the surface reconstruction. The relative transmittance spectra ($T_{rel}(\omega)$) shown in the next section were then calculated by dividing the sample spectra ($T_S(\omega)$) by the reference spectra ($T_R(\omega)$) as explained in section 3.2.1.

For all spectra (reference and sample) a resolution of 4 cm^{-1} was used unless otherwise noted. We changed the resolution from the previously used 8 cm^{-1} , as we planed on measuring C₇₀ peaks, some of which are only 14 cm^{-1} apart [46].

5.3 C₇₀ on Si(111)-7 \times 7

After we finished building our self made C_{70} evaporator, we needed to first test its stability and confirm the evaporation of C_{70} . Because of that we began by evaporating C_{70} on Si(111) wafers at RT at a rate of 1.3 nm per minute. The wafers were flashed beforehand to create their 7 × 7 reconstruction. FTIR spectra of these measurements are shown in Figure 5.2.



Figure 5.2: Relative normal transmittance spectra of C_{70} on pristine Si(111) at RT. (**a**) IR spectra of 0 nm to 40 nm C_{70} which were shifted relative to each other. The dashed lines and associated numbers slightly above the x-axis denote positions of prominent peaks. (**b**) Closeup of the 1429 cm⁻¹ peak at a 40 nm C_{70} coverage.

One can see the peaks, first the 1429 cm^{-1} peak, then slowly the smaller ones, developing linearly in height as the C₇₀ layer thickness increases. Comparing our measurement with the IR spectra and relevant peak positions of C₇₀ shown in Figure 5.3, we could identify six peaks in total.

Further testing the properties of C_{70} , we evaporated 5 nm C_{70} on a sample at 20 K with a rate of 0.13 nm C_{70} per minute. The spectrum is shown in Figure 5.4. Besides the large C_{70} peak at 1429 cm⁻¹ and CO₂ absorption lines around 2350 cm⁻¹ [47] we see a small transmission increase in the entire measurement region maximizing at around 2800 cm⁻¹ with additional 0.4% relative transmittance. This likely results from previously conducting Si-7 × 7 surface states now being isolating due to the influence of the C₇₀. This could be the result of electrons transferring from the Si(111)-7 × 7 surface (4.6 eV work function [42]) to the C₇₀, emptying the electronic band structure and reducing the amount of free charge carriers available.

These measurements demonstrate that our evaporator works as intended and that C70 is stable



Figure 5.3: FTIR measurements of purified films of C_{70} on KBr substrates at a resolution of 1 cm⁻¹. Experimentally measured C_{70} (**a**) IR spectra (modified from [46]) and (**b**) IR peak positions (ν_{IR} [cm⁻¹]) and relative intensity (I_{IR} [a.u.]). The outlined, blue peak at 1429 cm⁻¹ has by far the largest intensity and is the one we will use most to verify the presence of C_{70} . Modified from [46].

on Si(111)-7 \times 7 at RT and 20 K, paving the way for the C₇₀ doping measurements to begin.



Figure 5.4: Relative normal transmittance spectrum of C_{70} on pristine Si(111) at 20 K. The gray 100% line is again calculated by measuring the same sample twice at the same conditions and then dividing both spectra by each other to indicate setup stability. The blue line depicts 5nm C_{70} on Si(111)-7 × 7. Its noise is higher compared to the 100% line, as the blue line's measurement time was approximately three times shorter.

5.4 Au Chains on Si(111)

Since Au/Si(111)-5 \times 2 is the surface doped with C₇₀ in the following sections, measurements of the pristine system are used as a comparison point. The spectra of Au/Si(111)-5 \times 2 is depicted in Figure 5.5.



Figure 5.5: Relative normal transmittance spectra of Au/Si(111)-5 \times 2 at RT. The green line denotes polarization parallel to the chain orientation of the major domain ([110]), while the blue line represents orthogonal polarization ([112]).

Similar to Au chains on Si(553), the Au/Si(111)-5 × 2 shows the plasmonic resonance as expected. The absorption maximum is with about 1% weaker as HCWs, HCWs+0.05 ML and LCWs. A further difference is the diminished, but clearly visible, resonance for polarization orthogonal to the chains ([112]) at roughly the same wavenumber. This can be assigned to wires of the two other minor domains reaching equal chain length through partial step bunching, leading to the formation of wider terraces. These minor domains are always present for Au chains on Si(111) and are not sign of inadequate sample preparation. Quite the contrary, the different polarizations clearly reflect the anisotropy and one-dimensional property of this chain structure, indicating a well reconstructed Au/Si(111)-5 × 2 surface.

Additionally, a transmission decrease for wavenumbers larger than 3000 cm^{-1} is noticeable. This phenomenon is characteristic for the Au/Si(111)-5 × 2 and theorized to be caused by interband transitions [48].

5.5 C₇₀ Doping of Au Chains on Si(111)

Using the Au/Si(111)-5 × 2 chains from last section, we began the doping measurements by evaporating C_{70} at a rate of 1.7 ML_{5×2} per minute on the sample at RT. In Figure 5.6 FTIR measurements of the C_{70} doped Au/Si(111)-5 × 2 surface for different dopant amounts are shown.

Focusing first on the plasmonic absorption, it gradually decreases in strength and increases in width for higher amounts C_{70} doping. Furthermore, the resonance maximum shifts from about 800 cm⁻¹ without C_{70} to 1300 cm⁻¹ with 3 ML_{5×2}. This continues up to 0.75 ML_{5×2} when the absorption decreases more slowly until the difference between 1.25 ML_{5×2} C_{70} and 1.5 ML_{5×2} C_{70} becomes negligible. From 1.5 ML_{5×2} to 3.0 ML_{5×2} C_{70} barely anything changes, the entire spectra seemingly only shifts to a slightly higher transmittance, while its form stays the same.

We also performed an equivalent experiment at 20 K (with a C_{70} evaporation rate of $1.2 ML_{5 \times 2} = 0.39$ nm per minute). The results are shown in Figure 5.7. Comparing these spectra with Figure 5.6 the differences are remarkable, considering that the only difference in measurement conditions is the temperature at which the spectra were taken. While $0.125 ML_{5 \times 2}$ of C_{70} decreases the plasmonic resonance intensity significantly, additional C_{70} has considerably less effect. Even 30 nm, about 100 times the amount eliminating the resonance at RT, decreases the absorption maximum only by approximately 20% at 20 K.

Furthermore, measurements of the same $30 \text{ nm } C_{70}$ dopant two days later show that the absorption has completely vanished. This is not the result of the Au chains degrading normally, as they can sustain several days in UHV without sustaining damage of this magnitude [48].



Figure 5.6: Relative normal transmittance spectra of Au/Si(111)-5 \times 2 doped with various amounts of C₇₀ at RT. The dark green line with the deepest plasmonic absorption signal denotes the pristine Au wires. All other lines besides the grey 100% line represent various amounts of C₇₀ deposition on the Au chains.



Figure 5.7: Relative normal transmittance spectra of Au/Si(111)-5 × 2 doped with various amounts of C_{70} at RT and 20 K. Here, the dark green line also denotes the pristine Au wires. Blue, cyan, orange and purple represent highly varying amounts of C_{70} on top of the nanowires. The sample measured for the black lines was identical with the purple one, the only difference being the time passed since the measurement corresponding to the orange line was taken (half an hour for purple, two days for black) and the temperature (purple at 20 K and black at RT).

5.6 C₇₀ Doping Evaluation

In the viewpoint of electron transfer from Au chains to C_{70} our results indicate that this process saturates at RT for an evaporation amount of about $1.25 \text{ ML}_{5 \times 2} C_{70}$, when the entire plasmonic resonance vanishes. Considering that this is only an approximate value and that the real coverage of C_{70} on the sample at RT is approximately 10%-20% lower than the evaporation amount, it might be that the saturation takes place at $1 \text{ ML}_{5 \times 2} C_{70}$ present on the surface. This implies that each C_{70} is able to take up one electron from the Au chains.

Remarkably, the plasmonic resonance does not vanish at 20 K, regardless of the C₇₀ amount deposited on the surface. The signal only decreases below 80% of its original strength for C₇₀ doping at RT. Considering that temperature dependent energy fluctuations, such as Fermi edge broadening and the thermal energy k_BT , are of the order of meV [21], the electron transfer from Au chains to C₇₀ should behave identically at RT and 20 K. Instead, the temperature dependence is likely caused by the reordering of C₇₀ molecules to more energetically favorable positions near the chains, which enables the electron transfer. The energy needed for this reordering would constitute an energy barrier the C₇₀ molecules can only overcome at RT.

Besides electron transfer, a possible explanation for our findings is a structural destruction of the Au chains induced by the C_{70} . This is unlikely though, as C_{70} was chosen specifically because it is considered to be very inert and should not interfere with the chain structure. While a chain destruction would explain the absorption decrease and maxima shift, it does not explain the complete surface coverage needed to do so. One can roughly estimate the effect of C_{70} induced Au chain destruction as follows.

The average Au chain length of Au/Si(111)-5 × 2 is on the order of 100 nm [5] and each C₇₀ is roughly 1 nm wide [45], which means that the average chain is covered with 100 C₇₀ molecules once the surface is fully occupied. As a quasi one-dimensional system, the dispersion relation between plasmon energy E_P and plasmon wave vector $k_{||}$ Au/Si(111)-5 × 2 lies between the 1D ($E_P \propto k_{||} \propto 1/L$, where L is the chain length) and 2D $E_P \propto \sqrt{k_{||}} \propto \sqrt{1/L}$ case. Even assuming a fully two-dimensional dispersion, this implies a doubling of the plasmon energy for a quartered chain length. Bearing in mind the inherent statistical randomness of the adsorption site position, we can estimate that there are two random cuts needed to divide an Au chain in three parts that are all shorter than at least half of the original chain length. If every C₇₀ molecule destroys the chain part it adsorbs to, only 8% of a fully covered surface is needed to shift the plasmonic resonance position from 800 cm⁻¹ to 1600 cm⁻¹. This shift would be already larger than the shift from 800 cm⁻¹ to 1300 cm⁻¹.

The assumption that 100% of C_{70} molecules destroys the chain part it touches is completely arbitrary and the real percentage is currently unknown. In fact, if only 5% of C_{70} does so, the

absorption maximum would shift from 800 cm^{-1} to 1300 cm^{-1} for a fully occupied surface, exactly as observed. But the signal does not only shift, it disappears completely once full C₇₀ coverage is reached. Considering that a chain destruction of 5% should decrease the amount of free charge carriers by only 5% too, there is no reason for the signal to vanish entirely.

Electron transfer, on the contrary, would explain the resonance maximum shift to higher wavenumbers with increased C_{70} coverage very well. A similar effect has been observed for the doping of the Au/Si(111)-5 × 2 surface with additional electrons from the deposition of extra Au atoms on the surface. Here, too, this phenomenon can be attributed to the effective shortening of the average chain length, but not as a result of chain destruction. Instead, the formation of less conductive regions, due to the electron transfer from the Au chains into the C_{70} molecules, is the reason. There, the adsorbates did not destroy the chain structure and a comparable shift from approximately 700 cm⁻¹ to 1400 cm⁻¹ as well as the complete extinction of the plasmonic resonance was measured [5]. Considering the high similarity to our results, this strengthens the electron transfer hypothesis substantially.

6. Conclusion and Outlook

This thesis examined the optical and structural properties of pristine and doped atomic Au chains on Si substrates.

In the first part, HCW, HCW+0.05 ML, and LCW surface reconstructions were created. Their structure was analyzed via RHEED and FTIR, confirming the structural models and electronic behavior predictions by Song et al. [1], [38]. The plasmonic resonances of all three systems became sharper and stronger at lower temperatures, which was explained via less electron-phonon scattering. Measurements at room temperature and down to 20 K showed a continuous shift of the plasmonic resonance maximum to smaller wavenumbers for which the HCW's antiferromagnetic ground state could be ruled out as a main factor.

In the second part, C_{70} was evaporated on the Au/Si(111)-5 × 2 surface, where a decrease in plasmonic signal and shift to higher wavenumbers was observed. For a complete C_{70} surface coverage, the resonance vanished completely at RT and lost only 20% of its strength at 20 K. The temperature dependence is likely caused by the reordering of C_{70} molecules to more energetically favorable positions near the chains, which enables the electron transfer but is only possible at RT. This is assumed to be caused by electron transfer from Au chains to C_{70} .

While substantial results have been achieved, a couple of questions are left unanswered. Most notably, our estimation that each C_{70} molecule absorbs approximately one electron, depends greatly on the C_{70} amount evaporated, which was only roughly determined. Since C_{70} forms no structure visible in RHEED, one needs to measure the surface thickness directly. The most straightforward way to do so is to evaporate a sheet of a couple hundred nanometer of C_{70} and examine it with ellipsometry. Even though the so determined amount of deposition is significantly more accurate than using a geometrical Tooling factor [32], one faces a different problem afterwards. The sticking factor (the percentage of molecules reaching a surface that actually adhere to it and not desorb immediately) of C_{70} on pristine Si and Au should be lower than the sticking factor of C_{70} on other C_{70} [49]. Therefore, the first layer of C_{70} , for which knowing the exact coverage is essential, is deposited at a different rate than the following layers. Additionally, this is not measurable with the QCM, since there already is a several nanometer thick sheet of C_{70} on the QCM once the rate stabilizes enough to begin evaporating on the sample. Furthermore, C_{70} should adhere better at 20 K than it does at

RT as the sticking factor is temperature dependent. Because of this, one has to determine the surface coverage of a single C_{70} layer, which is not possible with ellipsometry or AFM measurements [49]. A possible solution to this problem might be STM measurements.

Shortly before this thesis was handed in, additional experiments regarding C_{70} doping were performed. Firstly, the plasmonic resonance of C_{70} doped Au chains did not reappear once cooled from RT to 20 K. If thermal fluctuations of the electron energies were a key factor in the signal decrease, the process should have been reversible. This result therefore seems to strengthen molecule reordering as explanation for the temperature dependence. Secondly, C_{70} was deposited on Au chains that were already doped with additional Au. Since C_{70} is an electron acceptor and additional Au an electron donor, both effects might cancel each other out. While a complete cancellation was not observed, the plasmonic signal after Au doping first increased slightly with C_{70} deposition up to $0.25 ML_{5 \times 2}$ when it started to decrease again. This behavior is closer to the interaction of two dopants canceling each other out than it is to a C_{70} induced structural destruction where an increase in signal through C_{70} can not be explained. Therefore, these new results seem to support the electron transfer hypothesis. Although much work is still to be done, further research in this area is promising.

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A. Appendix

A.1 Modification of the RHEED patterns

As mentioned, multiple Figure insets were modified to highlight the line structure and suppress noise of our RHEED pictures, making the streaks more visible. This modification is based on a Gimp Filter routine I designed. The following excerpt was originally written by me for the supporting information of the *Au Chains on Si*(553) paper currently in preparation.

The procedure is based on an edge detection algorithm called "Difference of Gaussians" (DOG). This algorithm works by using two different Gaussian blurs (depicted in Figure A.1(e)) and subtracting the resulting pictures.



Figure A.1: Modification process. (a) Original RHEED picture. (b) Image after DOG. (c) Image after DOG and desaturation. (d) Image after DOG, desaturation and intensity modulation. (e) Schematic zoom of the dashed square in (a) illustrating the Gaussian widths relative to the streaks. The change of intensity in the outer green circle relative to the inner one is big, while the change in the blue circles is small.

Each blur calculates the weighted average of each pixel and its neighborhood. The size and weight of this region is given by a normalized Gaussian distribution. Increasing the width of the Gaussians results in averaging over a larger number of pixels, each with a lower weight. Subtracting two such blurs with different widths effectively quantifies the change of intensity

and color between the two mask edges. If a pixel is near the edge of a structure, the intensity after applying the DOG will be large, if not, it will be small (Figure A.1(e)). Consequently, one can choose the size of the structures to highlight or suppress by varying the widths. By choosing the correct widths and applying the DOG on the entire image, the only structures left will be the streaks.

Not only has this approach the advantage of eliminating high frequency noise, it also decreases the intensity of low frequency structures that do not contribute to the pattern of streaks we want to highlight. After using the DOG filter, one gets a picture with the structure information desired, but also with low overall intensity, since the streaks are very weak (Figure A.1(b)). Upon desaturating the image (Figure A.1(c)), the intensity of all pixels is increased (Figure A.1(d)). By doing so, we maximize the visibility of the streaks, while minimizing the distortion of their relative intensity.

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Declaration

I hereby assure that I wrote this work independently and did not use any other than the denoted sources and tools.

Ich versichere, dass ich diese Arbeit selbstständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

Heidelberg, July 24, 2016

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