Studies on gold atom chains and lead nanowires on silicon vicinal surfaces

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Abstract. The Si(557) vicinal surface is produced from Si(111) by cutting the crystal at a small angle of 9.45° along the [112] direction. By a special cleaning process performed under ultra-high vacuum conditions, Si(557) displays a perfect grating structure consisting of parallel narrow terraces, each of them composed of a silicon plane with half unit cell of the Si(111)-7x7 reconstruction and a silicon row. Such an atomic grating makes it possible to get self-assembled atomic wires by decorating the surface with an optimal amount of 0.2 monolayer (ML) of Au. In the first step of the study, Si(557) is used as a template for fabricating of Pb nanowires by self-assembling in which the steps on the Si(557) surface provide the high-oriented diffusion channels for Pb wires growth. By means of polarized infrared spectroscopy the optical response of the Pb nanowires is investigated. As a major consequence of the interaction between infrared light and nanostructures, an antenna-like resonance appears. We found the shift of the antenna resonance frequency to lower wavenumbers due to the development of the nanowires in length under parallel excitation, whereas there is no significant change due to perpendicular excitation observed.

Keywords: Infrared spectroscopy, Pb nanowires, Au chains, vicinal surface.

1. Introduction
Si(557) and Si(557)-Au are the most popular vicinal surfaces derived from Si(111) and has attracted so much attention in the last few years since these structures are ideally suited for basic research on atomic wires with respect to Luttinger-Tomonaga-liquid behaviour and Peierls distortion occurring at low temperature due to electron-phonon coupling, e.g. [1, 2]. In general, the clean Si(557) surface consists of the parallel and well-ordered steps but they are only stable at the temperature above 600°C [3], hence, it is necessary to stabilize the surface. As it known from previous work [4], to totally stabilize the surface with gold, one has to obey the condition that every unit cell of the Si vicinal surface must be occupied by one Au atom. In case of Si(557), the optimal amount of Au is 0.2
monolayers (ML) and the reconstructed surfaces possess the co-appearance of atomic chains made of Au and Si parallel to each other on one terrace.

As a fully decorated surface, the Si(557)-Au composes of parallel diffusion channels that is an ideal substrate to grow parallel nanowires by self-assembling. The metallic nanowires made by this technique are single crystals with defect-free, highly oriented structures [4]. Under the appropriate excitation conditions by the external infrared (IR) electromagnetic field, these nanowire arrays show antenna-like response which can be assigned to the surface plasmon excitation [5-7]. The enhancement of the electrical field at the ends of the nanowires can be exploited for molecular sensing by tailoring the quantum interference between the resonance range of the antenna and the vibrational features of the molecules [6].

Within this short contribution, we would like to explain the experimental process to fabricate the clean Si(557) surface as well as Si(557)-Au where self-assembled Au chains display perfect one-dimensional atomic wires. Based on such careful surface preparation studies, the Si(557) surface is used to prepare Pb nanowires by taking advantage of the natural diffusion properties of Pb atoms, i.e. of the high mobility along the parallel channels. The shift of the antenna resonance frequencies under IR light makes it possible to control the development of Pb nanowires in length in situ [5].

2. Experimental detail

The experiments were performed under the ultra-high vacuum (UHV) conditions with a base pressure better than 1x10^{-10} mbar. The set up consists of a chamber connected with a nitrogen purged Fourier-transform infrared spectrometer (FTIR) (Bruker Tensor 27 with Mercury Cadmium Telluride - MCT detector) and a reflection high energy electron diffraction (RHEED) gun. Scanning tunnelling microscopy measurements (STM) were performed in a separated UHV chamber with a similar set up. Atomic force microscopy measurement (AFM) is done immediately after sample transfer to air.

Si(557) wafers with dimensions of 18x5x0.38 mm³ and a specific resistivity about 0.5 Ωcm were used as substrates. Prior to transferring into vacuum, the sample was prepared by ex situ cleaning with ethanol, acetone, and deionised water in the ultrasonic bath for 15 minutes for each solvent. This process removed dust from the wafer, but the natural silicon dioxide was still remaining. The cleaning process in UHV was performed by applying a direct heating current passing through the sample with the heating current parallel to the steps to avoid the electron migration effects (see [8] and references therein).

![Temperature response of the silicon wafer](image)

**Figure 1.** The temperature response of the silicon wafer (18x5x0.38 mm³, about 0.5 Ωcm) to a flashing current.

In order to determine the temperature response of the silicon sample to the direct heating current, a thermocouple (type K) was mounted on the Si sample with two spacers made of sapphire plates, mainly to insulate the thermocouple from the heating current. As can be seen in figure 1, at temperatures higher than 600°C, where the phonon-induced resistivity is dominant, an almost linear response is measured.
Figure 2. Heat treatment process of the Si(557)-Au fabrication.

Figure 2 shows the heating diagram that had been used to treat the silicon wafer in UHV and to decorate that sample with 0.2 monolayer of Au. The sample was first heated to 600°C and kept at that temperature for 20 hours. Afterwards, the wafer was heated up several times to 1200°C by heating pulses (so called flashing) with 5s for each, to remove the native silicon dioxide and the residual silicon carbide from the surface. The proper flashing current can be extrapolated from the response behaviour seen in figure 1. Within 30 s the sample was then cooled to 1060°C at which the step structures are most stable [3].

The most critical part in the sample preparation is to quench the surface from 1060°C to 830°C to avoid the formation of silicon carbide which can be produced on the fresh Si surface at temperatures higher than 900°C. The sample subsequently was kept at 830°C for 15 minutes to undergo the full transition from 1x1 phase to 7x7 reconstruction and then slowly cooled down to room temperature for the measurements or kept at 600°C for Au decoration, respectively. To capture the STM images, a special care had been taken to avoid the thermal drift by waiting at least one hour. Au and Pb evaporation were carried out with ceramic crucibles and heating filaments. Within the present study, one ML of Au corresponds to one ML of Si(111) in the topmost layer, consists of 7.84x10^{14} atoms/cm². One ML of Pb is estimated for Pb(111) layers the thickness which is 0.286 nm. The evaporated average thickness was estimated via the deposition rate measured with a water-cooled quartz crystal microbalance. Surface preparation steps were controlled by RHEED observations.

3. Result and discussion

Figure 3. A 100x100 nm² STM image of the Si(557) surface after the flashing and annealing procedure which was explained in figure 2. The achieved structure reveals parallel terraces with perfect periodicity of 5.9 nm within the accuracy of our measurement. The image was recorded at room temperature with a tunnelling current I = 0.2 nA and a sample bias U = -2.193 V.

The result of this publication came from the initial step of our co-operation project and it can be divided into two main parts: the first part dealing with the STM observation of the Si(557) surface and
Si(557) decorated by 0.2 ML of Au; the second part mentions the IR studies of self-assembled Pb nanowires on the bare Si(557) surface.

Figure 3 shows the STM image of a clean Si(557) surface, captured at room temperature with a tunnelling current of 0.2 nA and a bias voltage of -2.193 V. The surface reveals well-oriented steps with perfect grating structure at atomic scale. Every terrace consists of one silicon plane made of the halves of the Si(111)-7×7 unit cell. We found that as longer keeping the sample at 830 °C as more complete is the transition from the 1×1 to the 7×7 reconstruction. This is the main factor to form a vast and stable area of steps. Accordingly, the RHEED observation displayed very clear diffraction pattern (not shown here) of the 7×7 character.

Figure 4. STM image of Si(557)-Au with height profile (along the blue line) of the surface decorated by 0.2 ML Au. The new Au-induced surface structure with the periodicity of 2.1 nm was formed. The image was recorded at room temperature with the tunnelling current I = 0.2 nA and the bias voltage U = -2.154 V.

In an earlier work, Krawiec & Jalochowski claimed the existence of the double non-equivalent chain structure on one terrace forming the Si(557)-Au [9], as predicted before by a theoretical calculations by J. Crain et al. [10]. It is known that the electron wave function of the chains localizes at the end-atoms, so-called end states that influence the obvious chain length under STM current [11], depending on whether the scanning regime is for filled states or for emptied ones. Figure 4 shows the Au chains on the Si(557)-Au, recorded at room temperature with a tunnelling current of 0.2 nA and a voltage of -2.514 V. The height profile reveals that the periodicity of the structure was 2.1 nm, smaller than in the case of bare surface with 5.9 nm, which means that the surface had been reconstructed by the presence of Au chains. The bright spots that were distributed randomly on the surface originate from silicon adatoms. The co-appearance of the Au and Si chains can be identified via changing the tunnelling bias to see the emptied states.

As known, IR spectroscopy enables us to measure the optical conductivity of the metallic nanostructures by looking at the response of the free electron gas [7, 12, 13]. In the case of the nanowires, the appropriate polarized IR radiation with the optical frequencies could excite collective oscillation of the free electron gas in the range of the skin depth. The nanowires act as optical nanoantennae. As a consequence, it is possible to approximately describe such a scenario by the antenna relation at the fundamental resonance, i.e.

\[ <L> = \frac{\lambda(\mu m)}{2n_{eff}} \]  

(1)

This rough estimation does not take into account the influence of the detailed shape, and of the material of the nanowires. In equation (1), \(<L>\) is the average length of the nanowire array and \(\lambda\) the
excitation wavelength, and $n_{\text{eff}}$ the effective refractive index of the surrounding environment (here 2.52 [5]), respectively. For more precise relations see [5] and references therein.

The IR measurements in figure 5 show the development of the relative transmittance (reference is the substrate before Pb deposition) coming along with the shift of the antenna resonance during Pb evaporation. Already at 2 ML Pb, the resonance appears at 2500 cm$^{-1}$. The shift of the antenna frequency to lower wavenumbers (longer wavelength) reveals the corresponding growth of nanowires in length.

Figure 5. IR spectra recorded in situ during Pb evaporation from 0 to 10 ML. The shift to smaller wavenumbers is indicated. The antenna-like resonance was measured with parallel polarized electric field (parallel to the steps). 0 ML is the start of evaporation when the shutter of the Pb crucible was opened and 15 ML is the end of the deposition process when the shutter was closed.

The nucleation process at room temperature of the Pb nanowires was started via forming a wetting layer with the thickness of 1.3 ML (not shown here). Beyond this first initial stage the nucleation and aggregation of the Pb wires were developing. Hence, it can be inferred from figure 5 where at 2 ML the nanowires start to be excited by the external field that only 0.7 ML of Pb contributed to the formation of nanowires. A rough estimate gives an average length reaching of about 800 nm which means that there existed very long nanowires with very high aspect ratio. In a former work on Au-Si(335), a resonance length of only 500 nm at 2 ML is found under similar experimental conditions [5]. Compared to that situation, Si(557) seems to provide better ordered terraces with larger areas. If not taking into account the effects by different thermal treatment procedures in sample preparation, one can notice that the different intrinsic structure gives the differences in Pb diffusion and thus they influence the final length of the array via corner rounding diffusion and step separation.

It is also possible to estimate wire lengths from figure 5, like done in [5]. From figure 5 it turned out, that only length of nanowires from 800 nm (2500 cm$^{-1}$ at 2 ML) to 900 nm (2200 cm$^{-1}$ at 10 ML) occurs. This means also that after nucleation the growth rate in the width of the wires was faster than that in length. Since the final structure is defined from the very beginning stage of the nucleation process, it is reasonable to notice that both the surface energy and the sample preparation (including evaporation rate, substrate temperature) defined the nucleation density, and therefore influenced also the final average length in the nanowire arrays.

Figure 6 displays the different responses of the lead nanowires to the incoming electrical field for two different orientations: parallel and perpendicular to the long axis of the nanowires. The transmittance spectrum in case of perpendicular polarization looks similar to spectra of metal island films regarding the lower transmittance (i.e. higher extinction) at the higher wavenumbers. The antenna resonance peak clearly appears for parallel excitation. The inset shows the AFM morphology of the lead wires (taken right after the sample had been transferred to the air).
4. Conclusion
In summary, we demonstrated the first stage of our studies on Au atom-chains and Pb nanowires on the Si(557) surface by STM and IR measurements. Si(557) and Si(557)-Au revealed nearly ideal atomic chain structures which are well-suited for fundamental research on low dimensional system such as atom chains and nanowires. The Pb nanowires grown on such surfaces behave like IR optical antennae under the appropriate excitation regime.

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