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Electronic end-states in platinum atom chains

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ABSTRACT

We investigated electronic surface states in platinum atom chains grown on Ge(001). Scanning tunneling microscopy/spectroscopy was used to record the electronic landscape on atomic platinum chains. High-resolution spatial maps of individual Pt-dimers near the termini of the chains revealed a difference in the electronic structure between the end dimer region and the chains bulk region. Experiments and tight-binding calculations show a one-dimensional character of the electronic states, decaying rapidly into the chains.

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1. Introduction

Nanowires, nanoscopic structures with a very high aspect ratio, can be assembled on substrates using various material compositions. On the forefront of these, silicon (Si) and germanium (Ge) are the most widely used substrates. A broad range of possible materials is known to induce the growth of nanowires on Si and Ge. Under high investigation are nanowires, induced from rare earths [1], transition metals and post-transition metals [2]. Especially 5d transition metals, such as gold (Au) [3–6], platinum (Pt) [7] and iridium (Ir) received much attention over the last decade. Pt atom chain assemblies are ideal systems to study, for instance, quantum confinement [8–10] and Peierls instabilities [11, 12].

The structural and electronic properties make the nanowire arrays ideal anchors for molecules, that are of interest to molecular electronics. By capturing a single molecule between a nanowire and the apex of a scanning tunneling microscope tip the transport properties of an individual molecule can be determined [13–18].

Low dimensional electronic states have been of great interest in nanoscience and nanotechnology [19–22]. Quantum dots [23–26] and atomic nanowires are on the forefront of science of low-dimensional physics. While quantum dots are mainly used to store and release low quantities of electric charge, nanowires are heavily investigated because of their importance for electronic transport [27,28]. However, one-dimensional atomic wires can also host zero-dimensional electronic states. Crain and Pierce studied Au nanostructures on Si (553) and showed the existence of zero-dimensional end-states at the edges of these structures [29].

In this work we demonstrate an end-state effect of the electronic states in proximity to the termini inside Pt atom chains. These self-assembling chains were grown on a Ge(001) surface [30,7,8,31,32]. These effects are investigated with scanning tunneling microscopy and spectroscopy (STM and STS), supported by tight binding calculations to study the origin of the state and its dimensionality.

2. Experimental details

The experiments were performed in a dedicated ultra-high vacuum system equipped with an Omicron low-temperature STM. The Ge(001) samples are cut from nominally flat, 3 in. by 0.3 mm, single-side polished, nearly intrinsic n-type wafers. After cutting, the samples were thoroughly cleaned with isopropanol alcohol, before inserting them into the ultra-high vacuum system. First the Ge(001) samples were outgassed for at least 12 h at a temperature of 750–800 K. Subsequently, we cleaned the Ge(001) samples by applying cycles of argon ion bombardment (500 eV, 20 min), followed by annealing at temperatures of 1100 (\pm 25) K. After several of these cleaning cycles, the Ge(001) samples were atomically clean and exhibited a well-ordered dimer reconstructed surface [33,30]. Subsequently, an equivalent of 0.2–0.5 monolayers of Pt was deposited onto the substrate at room temperature. Pt was evaporated by resistively heating high purity Pt (99.995%) wires, wrapped around a tungsten wire. Immediately after deposition the sample was flash-annealed to 1050 (\pm 25) K three times and then cooled down to room temperature before placing it into the STM for imaging. All experiments are performed at 77 K.

3. Results and discussion

Fig. 1 shows a scanning tunneling microscope image of an array of self-organizing atomic Pt chains on Ge(001). The most abundant

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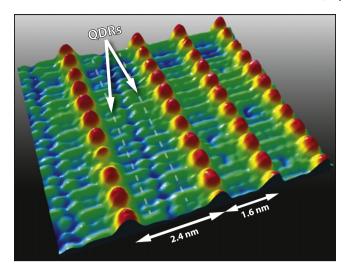


Fig. 1. STM image of Pt atom chains on a Ge(001) surface with separations of 1.6 nm and 2.4 nm. Quasi dimer rows are visible in the troughs. The image was recorded at 77 K at a setpoint current of 0.5 nA and a bias voltage of 1.5 V.

nearest-neighbor spacing between the atomic Pt chains is 1.6 nm, however larger spacings (e.g. 2.4 nm) can occur [34,7]. In this low temperature STM image, the spacing of 2.4 nm reveals that in every second Ge-Ge dimer one Ge atom is replaced by a Pt atom, forming the so called quasi dimer rows (QDRs) [7]. The adjacent QDR shows the same alteration, however the registry is shifted by one dimer, giving the configuration a zipper-like appearance.

At room temperature, the atomic chains are comprised of symmetric dimers yielding a $2\times$ periodicity. Scanning tunneling spectroscopy measurements reveal that the atomic chains are metallic at room temperature. Upon cooling down to cryogenic temperatures the atomic chains, when present in an arrangement of multiple chains (see Fig. 1 for an example of such a patch of chains), undergo a doubling of the periodicity and the density of states at the Fermi level is suppressed [11]. This transition is interpreted as a Peierls transition. The Peierls phase transition temperature is intimately related to the coupling to the environment. The weaker the coupling, the lower the Peierls phase transition temperature. The Peierls transition temperature for an ideal 1D system is 0 K [12]. For chains not present in patches, i.e. isolated chains with no neighboring chains, the transition temperature can be lower than 4.7 K, since isolated Pt atom chains still exhibit a $2\times$ periodicity at 4.7 K.

We investigated the electronic landscape of the Pt chains at 77 K. For this experiment, we focus on a small group of nanowires within a larger patch. The selected area can be seen in Fig. 2. Pt atoms, missing within the chain, restrict the wires in length. At the selected location, multiple short wires in close proximity to each other can be found, that all have a missing atom or dimer along the chains. This makes it possible to study the electronic states at the end of and along many smaller nanowires within one experiment, ensuring uniform experimental conditions.

An STM image of several Pt chains is shown in Fig. 1. The typical distance between the individual nanowires is 1.6 nm. This distance can be larger, however it will always be a multiple of 0.8 nm at a 1.6 nm minimum, due to the surface reconstruction on the underlying substrate. The nanowires can accumulate to large, well-defined patches or appear in small groups. This is influenced by the density of defects on the surface and the coverage of Pt.

Scanning tunneling spectroscopy was performed on this specific region, with high spatial resolution, in order to achieve satisfactory statistics. For this the tip was parked at every point on a 75 by 75 point grid raster. The feedback loop was then switched off at each grid point and the voltage was swept between 1 V and -1 V. The setpoint for the measurements was always 1 V at 180 pA tunneling current. Six wires have been selected for a detailed investigation of their electronic

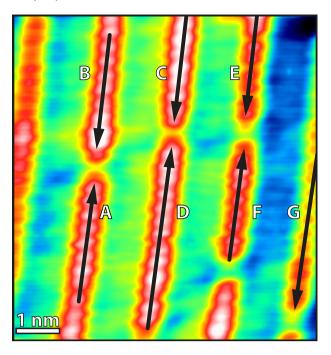


Fig. 2. A 7 nm \times 7 nm STM image of a set of Pt atom chains labeled A to G, recorded at 77 K. STS was performed on each of these wires in order to examine the spatial dependence of electronic states in proximity to the end of the wires (end dimer is indicated by the arrow head). The bias voltage was 1 V for a current setpoint of 180 pA.

characteristics, in the center of the image. For this, we divided each wire into its respective dimers and average all the spectroscopy data for each dimer. For the three top wires (B, C and E in Fig. 2) the "End Dimer" was defined as the last dimer at the bottom of the wire. All subsequent dimers in the chain are labeled by position relative to the end dimer (e.g. "1st Bulk Dimer" to "4th Bulk Dimer 4") upwards from the end dimer for the wire B, C and E. Similarly the end dimers of the three bottom wires (A, D and F in Fig. 2) were defined as the top most dimers in the chains with the bulk dimers counting up in the downwards direction. All of the I(V) curves were averaged for each respective dimer.

Several peaks in the local density of states (LDOS) can be identified on the positive bias side of the spectra. The LDOS was determined by normalizing the differential conductivity dI(V)/dV with I(V)/V. Two peaks are most pronounced: one peak is located in a bias window between -200 mV and -310 mV (Peak 1 in Fig. 3). The other (Peak 2 in Fig. 3) is located between -720 mV and -650 mV. The most remarkable aspects of these crests are, that the maximum of Peak 1

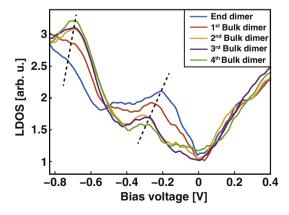


Fig. 3. LDOS measurements performed on Pt atom chains. Each curve represents the LDOS of a specific dimer in the chain from the end dimer counting up to four bulk dimers. The measurements were taken at a setpoint current of 180 pA and voltage of 1 V.

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