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Etching of silicon nanowires on Ag(1 1 0) by atomic hydrogen

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ABSTRACT

Scanning Tunnelling Microscopy, High Resolution Electron Energy Loss Spectroscopy and High Resolution X-Ray Photoelectron Spectroscopy have been used to study the adsorption of atomic hydrogen onto Si nanowires grown on Ag(1 1 0). We demonstrate that the hydrogen strongly interacts with the Si nanowires modifying their structural and electronic properties. Hydrogen atoms etch the Si nanowires and eventually lead to their complete removal from the Ag(1 1 0) surface.

1. Introduction

One-dimensional (1D) structures are receiving a great deal of interest because of their potential use for nanotechnology and the ability they provide to understand the fundamental physics of low-dimensional systems.

It has been recently shown that it is possible to grow massively parallel 1D Si nanowires (SiNWs) by evaporation of silicon atoms onto a Ag(1 1 0) surface [1,2]. This system has been thoroughly studied experimentally by means of Photoelectron Spectroscopy (PES), Scanning Tunnelling Microscopy and Spectroscopy (STM and STS, respectively), low-energy electron diffraction (LEED) and Auger Electron Spectroscopy (AES) as well as by density functional theory [1–5]. It has been asserted that such SiNWs present a metallic character and that they can be used as a template surface for molecular adsorption [1,3–5]. Selective adsorption of specific molecules onto this type of SiNWs can lead to the formation of organic nanowires and therefore modify the electronic properties of the SiNWs themselves [5]. Also, the oxidation of such SiNWs has been studied and showed a gap opening upon oxygen adsorption revealing the formation of a transversal internal nanojunction [6]. In the same aim, we intended to passivate the SiNWs with atomic H and compare the reactivity of such 1D Si nanostructures with those of the well known Si(1 1 1) and Si(0 0 1) surfaces.

For this purpose, the structural, vibrational and electronic properties of hydrogenated SiNWs were probed both at the PIIM laboratory in Marseille (France) using LEED, STM, High Resolution Electron Energy Loss Spectroscopy (HREELS) and at the MAX-Lab synchrotron radiation facility in Lund (Sweden) by means of High Resolution Photo Electron Spectroscopy (HRPES).

2. Experimental setup

All experiments have been carried out under ultra-high vacuum conditions (UHV). HREELS, LEED and STM measurements were performed at the PIIM laboratory in Marseille whereas HRPES measurements have been carried out at beamline I311 of the Max-Lab synchrotron radiation facility. The resolution in HREELS, determined from the full width at half maximum (FWHM) of the elastic peak, was 6 meV. While the total HRPES resolution, determined from the width of the Fermi step, was 60 meV. Further details on the beam line are given elsewhere [7]. In the case of Scanning Tunnelling Microscopy, the images were obtain using tungsten tips made from a tungsten wire following a classical electrochemical etching procedure in a solution of sodium hydroxide 2 M. In both places, the surface of a Ag(1 1 0) single crystal (purchased from Mateck) was prepared by several cycles of Ar ions (Ar^+) sputtering (1000 eV) and annealing (620 K). SiNWs were obtained by deposition, at room temperature (RT), of a submonolayer of Si atoms onto a freshly cleaned Ag(1 1 0) surface, as previously described [1,2,4,5]. At the PIIM laboratory, the hydrogenation of the SiNWs was performed using an atomic hydrogen source which consists of a tungsten capillary heated up to 2600 K by electron bombardment, providing a nearly 100% H_2 cracking efficiency. A first SiNWs sample was exposed at RT to a flux of 5×10^{13} hydrogen atoms per

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second for 200 s while another one was exposed also at RT to a flux of 2×10^{14} hydrogen atoms per second for 200 s. At MAX-Lab, a hot tungsten filament was used to dissociate molecular hydrogen. The exposure of the SiNWs has been estimated via the background pressure of molecular hydrogen monitored with an ion gauge. There, the samples have been exposed at RT to certain flux of atomic hydrogen resulting from the dissociation of: 12 Langmuirs (L) of molecular hydrogen (1×10^{-7} Torr during 120 s) for the first one and 300 L (1×10^{-6} Torr during 300 s) for the second one.

For the fitting procedure of the XPS data, the background was synthesize a simple polynomial function using and the line shape used for the main lines was a Doniach–Sunjic line shape [8,9]. In all cases the fitting parameters for the spin–orbit splitting, the asymmetry parameter and the branching ratio were kept constant and, respectively, equal to 0.09, 0.5 and 0.6 eV. The FWHM used were typically 180, 140 and 250 meV for each peak of the S1, S2 and S3 doublets.

3. Results and discussion

Fig. 1 shows two diffraction patterns recorded at 44 eV primary beam energy corresponding, respectively, to the clean Ag(1 1 0) surface (Fig. 1a) and a submonolayer of SiNWs (Fig. 1b). Fig. 1a clearly exhibits the typical rectangular (1×1) pattern of the clean Ag(1 1 0) surface. The two arrows represent the basis vectors of the reciprocal unit cell. Fig. 1b shows a diffraction pattern of the surface with the SiNWs. Superimposed to the (1×1) of the Ag(1 1 0) (bright diffraction spots), one can observe discontinuous lines extending along the [0 0 1] direction demonstrating the formation of a $(2 \times n)$ superstructure (with n an integer) of the Si atoms adsorbed onto the Ag surface. This shows that at submonolayer coverage, the Si atoms adopt a 1D long-range order along the $[\bar{1}\,1\,0]$ direction with a $2\times$ periodicity along this direction, as has already been reported [1,2]. This structural conformation of the Si atoms adsorbed onto the Ag(1 1 0) is confirmed by means of STM as it is depicted in Fig. 2. The latter shows a 70 nm × 80 nm STM image of a submonolayer of SiNWs obtained at room temperature. Each NW is 13 Å wide, aligned along the $[\bar{1}\,1\,0]$ of the Ag(1 1 0) and presents bright protrusions particularly well resolved in the top-right inset of Fig. 2 which corresponds to a zoom-in of 10 nm × 10 nm. Even if not well resolved, one can claim, according to previous theoretical and experimental results, that these protrusions correspond to Si dimers [2,3]. Each dimer is distant from another one by 0.56 nm along the $[\bar{1}\,1\,0]$ direction, a length which is approximately twice the value of the Ag(1 1 0) lattice parameter along this direction ($a_{[\bar{1}\,1\,0]}$ = 0.29 nm). This periodicity matches the periodicity observed previously by LEED. Even though there

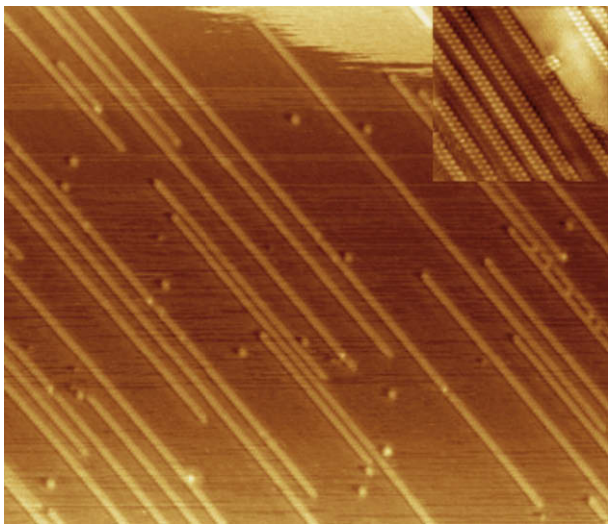

Fig. 2. 70 nm × 80 nm STM image of SiNWs adsorbed onto Ag(1 1 0) at RT, I_t = 0.47 nA, V_{bias} = −600 mV, filled states. The top-right inset corresponds to a zoom-in of 10 nm × 10 nm, I_t = 0.32 nA, V_{bias} = −20 mV, filled states.

is not yet a well known atomic structure of these SiNWs, several models have been proposed, discussed and described [1–5]. The common point of these models is that the SiNWs are made of a double layer of Si atoms adsorbed onto a Ag(1 1 0) surface. The top Si layer is formed by Si dimers while the bottom layer is constituted of Si atoms directly adsorbed onto the Ag surface.

As mentioned above, the purpose of the work presented here is to probe the reactivity of such SiNWs upon hydrogen adsorption. To do so, we exposed the SiNWs described previously to atomic hydrogen and probed their structural, vibrational and electronic properties by means of LEED, STM, HREELS and HRPES. Fig. 3 shows three typical high-resolution electron energy loss spectra of bare SiNWs adsorbed onto Ag(1 1 0) (blue line) then exposed to a flux of: 5×10^{13} hydrogen atoms per second for 200 s (red line) or 2×10^{14} hydrogen atoms per second for 200 s (black line). These spectra were recorded at 3 eV primary beam energy and in specular direction with an incident angle of 61° from the surface normal. On the figure, the main peak corresponds to the elastic peak and is centered at 0 meV loss energy. No specific vibrational mode is detected on the spectrum related to the SiNWs. This indicates that the SiNWs are clean besides there is no clear evidence that the adsorption of the SiNWs modifies the surface electronic properties in this energy range. After having exposed the SiNWs to 5×10^{13} hydrogen atoms per second for 200 s, several loss features, labeled

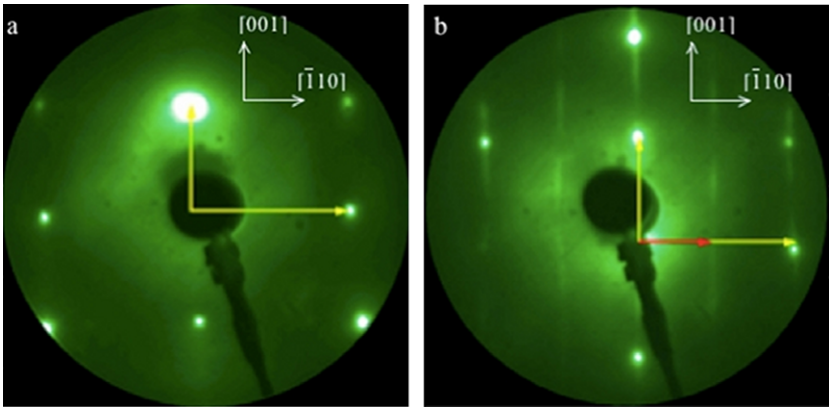

Fig. 1. LEED patterns recorded at 44 eV primary energy: (a) (1×1) of a clean Ag(1 1 0) substrate; (b) $(2 \times n)$ superstructure of SiNWs adsorbed onto Ag(1 1 0) at RT.