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Oxidation of the 8 × 8-reconstructed β-Si_3N_4(0 0 0 1) surface: A photoemission study

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ABSTRACT

The thermal oxidation of the β-Si_3N_4(0 0 0 1)-8 × 8 surface has been carried out. The spectroscopic characterization has been performed by high resolution core-level and by angle-resolved photoemission spectroscopy. Our findings demonstrate that the surface shows a low but clear reactivity with oxygen. The known resonance ascribed to the 8 × 8 reconstruction results strongly affected by the oxygen dosing, demonstrating the involvement of the topmost nitride atoms.

1. Introduction

Thermal nitridation of the 7 × 7-reconstructed Si(1 1 1) surface, when performed at temperatures exceeding 1050 K, gives rise to the β-Si_3N_4(0 0 0 1) phase, showing up a 8 × 8 surface reconstruction. Low Energy Electron Diffraction (LEED) and Scanning Tunneling Microscopy (STM) measurements on the 8 × 8 structure have been undertaken to unveil this complex structure [1–8]. A peculiarity of β-Si_3N_4(0 0 0 1)/Si(1 1 1) system is that the nitride film is crystalline and ultra-thin due to the self-extinguishing property of the nitridation process [9,10]. It is already known that the β-Si_3N_4(0 0 0 1) can act as a prototypical passivation layer, suppressing the metal-Si reaction. Indeed, studies reporting on the interaction of the nitride with Au, Co and Fe (among the most reactive elements with silicon [11–15]), demonstrate the ability to prevent the formation of silicides for temperatures up to 600 K [13,16]. However, no studies have addressed the behaviour of this system against oxygen, although few papers focussed on the interaction of oxygen with the bulk structure of the nitride in its β-phase [17–20].

The knowledge of the oxidation process of this surface may provide fundamental information in many fields of applications of silicon nitride, since this can be the onset of controlled surface functionalization. In biosensing devices, silanization of the native SiO_2 layer on the Si_3N_4 film is the prevalently used method for immobilization of biomolecules [21–24]. However, a major problem is that the resulting Si—O—Si—C linkage is prone to hydrolysis [25,26]. Therefore, it is an issue to obtain a passivated surface with high control over the oxidation process as well as on the reactivity of the resulting oxide. Si_3N_4 is also a material for in vivo applications [27,28], where biocompatibility is an opportunity which can be seized by covalent functionalization via oxidation onset.

To this purpose, we aim here at investigating the first stages of the oxidation of the nitride surface by taking advantage of

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the resonance recently reported in [29]. This resonance has been attributed to topmost atoms of the 8 × 8-reconstructed surface, so that a treatment of the surface (i.e. thermal oxidation) should affect the lineshape of the valence band. Angle resolved photoelectron spectroscopy (ARPES) as well as high resolution core-level photoelectron spectroscopy will be employed in the study.

2. Experimental

High resolution core-level spectroscopy and ARPES measurements were performed at the UHV photoemission end station of the TEMPO beamline [30] at the SOLEIL synchrotron radiation source. Linearly polarized photons from the Apple II type Insertion Device (HU44) were selected in energy using a high resolution plane grating monochromator with a resolving power $E/\Delta E = 5000$. The end-station chamber (base pressure 10^{-10} mbar) is equipped with a modified SCIENTA-2002 electron analyzer with a delay-line 2D detector which optimizes the detection linearity and signal/background ratio [31]. The overall energy resolution was better than 200 meV. The photon beam impinged on the sample at an angle of 43°, and photoelectrons were detected on an angular range up to 12°.

Si(1 1 1) samples were cut from *n*-type (P-doped) silicon wafers with resistivity $\rho \simeq 0.1$–$1\ \Omega$cm. The surface was out-gassed at 700 K for several hours using direct resistive heating. The sample was cleaned by repeated flashes of several seconds at 1500 K at a base pressure of $\sim 3 \times 10^{-10}$ mbar, leading to a sharp 7 × 7 LEED pattern. The 7 × 7-reconstructed surface was held at a temperature of approximately 1050 K and exposed to 50 L of NH_3 gas flow. The thermal nitridation induces a 8 × 8 reconstruction as verified by LEED, according to the literature [13]. Subsequently, thermal oxidation has been carried out by dosing molecular oxygen for 10 min at a pressure of 8×10^{-8} mbar, i.e. almost 30 L, while keeping the sample at 850 K. No carbon signal was detected on the surface, neither before nor after oxidation.

3. Results and discussion

In Fig. 1, we report the Si2p high resolution core-level spectra taken with 140 eV photon energy. The spectrum plotted with blue crosses has been recorded on the bare surface of the silicon nitride, while the one in solid red has been recorded on the oxidised surface. The spectra have been normalised to the background towards low binding energy. An important variation of the intensity is recorded by comparing the spectra. Two prominent features are evident: between 98 and 101 eV binding energy the spectra represent mainly the part related to the bulk silicon, while the feature above 101 eV is generally ascribed to the silicon atoms in nitride environment [12,32–34]. Upon oxidation a general attenuation is recorded, although to a different extent (when comparing the nitride-related, to the substrate-related part of the spectrum). This evidence is explained by the thinness of the nitride layer with respect to the sampling depth, which amplifies the adsorbate attenuation. The spectra show essentially the same lineshape and width: this is why any attempted decomposition of the spectra would be meaningless. Nonetheless, a qualitative analysis has been performed by subtracting the spectra (shown below the core level spectra in Fig. 1). The negative intensity (*a′* and *a″*) at about 99 and 102 eV is ascribed to the simple attenuation due to the oxygen adsorbate, since the energy values roughly correspond to the energy distance of +2.8 eV between the Si^{4+} nitride state and the bulk silicon [12]. The positive intensity (in correspondence of the letters *b*–*d*) is related to the energy values where the oxygen generates new components due to the interaction with the nitride surface. *b* and *c* fall at about 100 and 103 eV, typical binding energy values related to Si^{1+} and Si^{4+} oxidation states [35,36], respectively. The intensity *d* remains an unresolved component which could be ascribed to a ternary compound Si—N—O or surface defects.

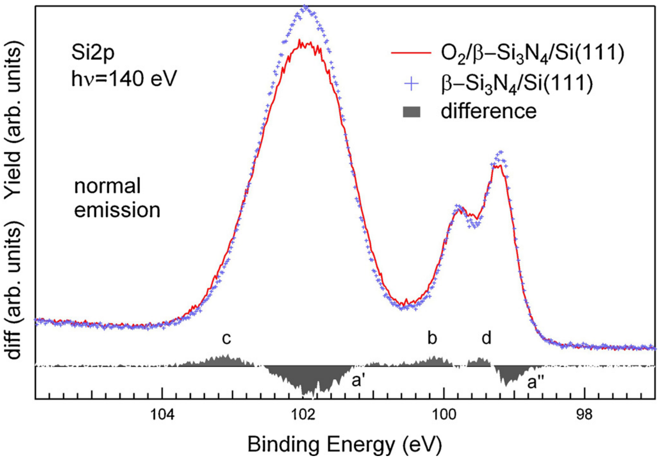

Fig. 1. High resolution core-level photoemission spectra of the β-Si_3N_4(0 0 0 1)/Si(1 1 1)-8 × 8 as well as the O_2/β-Si_3N_4(0 0 0 1)/Si(1 1 1) surfaces. The spectra have been recorded at 140 eV photon energy. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

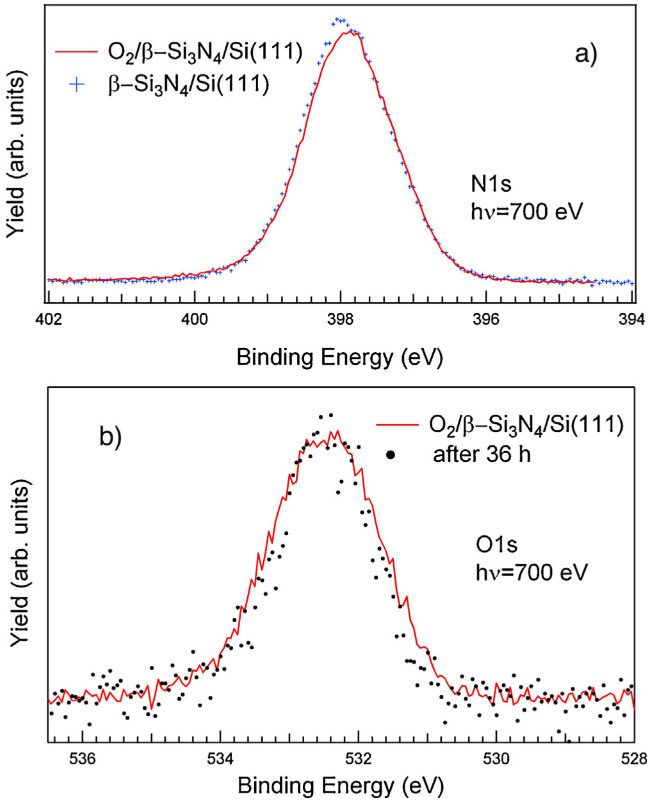

Fig. 2. N1s and O1s high resolution core-level spectra recorded at 700 eV photon energy, in panel (a) and (b), respectively. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

In Fig. 2(a) and (b), we report the N1s and O1s spectra, respectively, taken at a photon energy of 700 eV, before and after oxidation. Only a slight intensity difference is recorded between the two spectra, while the lineshape is identical. As for the O1s core level spectra shown in Fig. 2(b), the peak falls at about 532.5 eV, i.e. in SiO_x-like environment [37]. In this respect, we can rule out the sole physisorption of molecular oxygen whose signature is above