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In-situ formation of SiC nanocrystals by high temperature annealing of SiO_2/Si under CO: A photoemission study

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ABSTRACT

We have studied CO interaction with SiO_2/Si system at high temperature (~1100 °C) and 350 mbar by core-level photoemission. Even for short annealing time (5 min) the signal from Si2p and C1s core levels shows a clear change upon CO treatment. Shifted components are attributed to formation of SiC. This is confirmed by TEM imaging which further shows that the silicon carbide is in the form of nano-crystals of the 3C polytype. Photoemission spectroscopy moreover reveals the formation of silicon oxicarbide which could not be evidenced by other methods. Combining these results with previous Nuclear Resonance Profiling study gives a deeper insight into the mechanisms involved in the nanocrystals growth and especially for the reaction equation leading to SiC formation. We show that CO diffuses as a molecule through the silica layer and reacts with the silicon substrate according the following reaction: $4\ CO + 4\ Si \rightarrow SiO_2 + 2SiC + SiO_2C_2$.

1. Introduction

Silicon carbide (SiC) is a well-known wide band gap semiconductor having interesting properties for high temperature, high power and high frequency applications. It can work under harsh conditions and is also biocompatible [1]. As a consequence, the growth of SiC films for example by Chemical Vapor Deposition or Molecular Beam Epitaxy has been extensively investigated for the last decades [2–4]. But more recently, the interest for silicon carbide also turned to the growth of nanocrystals (nc). Indeed, when SiC is in the form of nanocrystals, it combines the exceptional intrinsic properties of the material with nc properties giving rise to new characteristics and thus potential applications. Therefore, SiC nc are widely studied for optoelectronics applications thanks to strong photoluminescence in the blue to UV range due to quantum confinement [5]. They also are of interest for non-volatile memories [6], non-linear optics [7] and fluorescent biological labels [8].

Different techniques are used to grow these nc: carbon implantation [9], laser CVD [10] or electrochemical etching [8] for example. Besides all these techniques, it was previously shown that an easy way to obtain cubic SiC nanocrystals is to anneal SiO_2/Si samples under a few hundreds of mbar of carbon monoxide (CO) at temperature around 1100 °C [11]. Nc grown by this technique were studied from a morphological point of view by TEM and SEM, evidencing the influence of different parameters such as the substrate orientation, CO pressure or the annealing time on the shape, size and nucleation density of the nc [12]. We also performed Nuclear Resonance Profiling (NRP) experiments on this system and showed that CO diffuses as a molecule throughout the silica layer and reacts with silicon to form SiC [13,14].

However, no information about the chemical state of oxygen atoms incorporated at the interface and thus about the exact equation of reaction could be achieved. In that context we performed core-level photoemission experiments using synchrotron radiation to study in-situ CO interaction with SiO_2/Si samples. The changes of Si2p and C1s core levels upon CO treatment at high temperature (around 1100 °C) for 350 mbar CO pressure were systematically checked. They reveal the formation of silicon carbide located at the SiO_2/Si interface, as confirmed by TEM measurements on the same sample. TEM results further show that SiC is crystalline of the 3C type. More interestingly, photoemission gives the first evidence that the oxygen atoms incorporated in the sample further oxidize the Si substrate, and form SiO_2 as well as SiO_2C_2 oxicarbide, which could not be evidenced by other methods. By combining these new results with previous NRP studies, we can propose a scenario for the formation of SiC nc: CO diffuses as a molecule through the silica layer and react with the Si substrate, giving $4\ CO + 4\ Si \rightarrow SiO_2 + 2SiC + SiO_2C_2$.

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2. Materials and methods

We performed core-level photoemission experiments on the TEMPO beamline at the SOLEIL synchrotron facility in Saint-Aubin, France. The resolving power E/ΔE of this beamline is better than 10,000 for the whole energy range (~50 to 1500 eV). The analysis chamber is equipped with a Scienta-2002 electron analyser. In order to perform in-situ treatments in the same temperature and CO pressure conditions required for 3C-SiC nc growth, we specifically designed a small preparation chamber connected to the existing experimental setup. This UHV preparation chamber allowed to anneal SiO_2/Si samples by direct current heating to temperature around 1100 °C and under several hundreds of mbar of CO. The temperature was measured using a pyrometer. During the treatment, the preparation chamber is isolated from the rest of the experimental equipment. Liquid nitrogen trap was used to maintain water level below 5 ppm. Then, the gas is pumped out and the sample is transferred under UHV conditions to the analysis stage, avoiding thus any carbon contamination.

Previous studies revealed that nc growth occurs at the SiO_2/Si interface and that SiO_2 layer is required to obtain good quality nc. To probe this region of interested with XPS we need a thin oxide layer so that the mean free path of the photoelectrons will be large enough to allow photoelectrons to go through the SiO_2 layer and to be detected. Thus, we first grew ex-situ 4 nm thick SiO_2 layer on Si(111) substrates by chemical oxidation. The thickness of the oxide layer was confirmed by Nuclear Reaction Analysis (NRA). In such a case, by changing the incident photon energy, we are able to probe the sample from the SiO_2 surface to the SiO_2/Si interface and the Si bulk.

Before any CO treatment, the oxidized samples were outgassed in UHV for a whole night at low temperature in order to remove any carbon contamination.

The high purity carbon monoxide is provided by Alphagaz. In the present results, the sample was annealed under 350 mbar of CO for 5 min at 1100 °C.

The base pressure in the analysis chamber remained in the low 10^{-10} Torr during the whole experiment.

The microstructure and morphology were investigated by transmission electron microscopy (TEM) in cross-section and in plan-view as well. Transparent samples were prepared by Ar ion beam thinning. For the conventional TEM characterizations a Philips CM20 microscope was used at 200 kV. High resolution images were taken using a JEOL JEM 3010 transmission electron microscope with point resolution of 0.17 nm.

3. Results and discussion

Fig. 1 displays the Si2p core level photoemission spectra measured on SiO_2/Si sample before any CO treatment for a photon energy of 700 eV. Using a standard least-square-fitting procedure, the spectra are decomposed into components consisting of spin-orbit split Voigt functions.

A Lorentzian width of 85 meV and a spin-orbit splitting of 602 meV are used for all components [15]. Two components (A and B) in Fig. 1 are forming the Si2p peak with binding energy of 102.9 and 99 eV and Gaussian widths of 1.5 eV and 0.5 eV respectively. These two components can be attributed to the SiO_2 layer and bulk Si. No suboxide can be detected showing that the interface is abrupt. Before the CO treatment only a weak signal from C1s could be detected at photon energy of 350 eV (most surface sensitive), showing very low surface contamination (not shown here).

We now focus on SiO_2/Si sample after annealing for 5 min under 350 mbar of CO at 1100 °C. Fig. 2 shows typical Si2p spectra for such sample and for different incident photon energies varying from 150 to 800 eV. Clear changes compared to the clean surface can

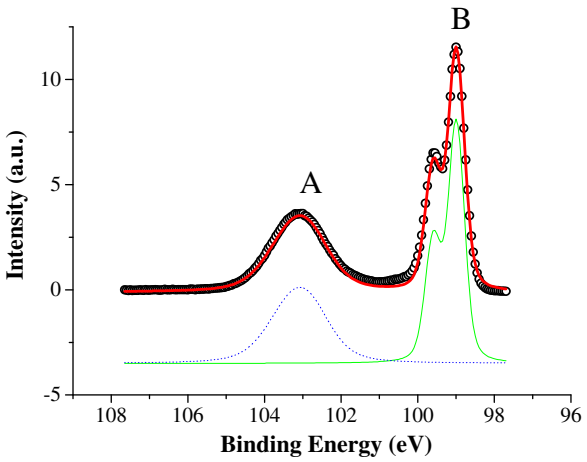

Fig. 1. Si2p core-level spectrum taken on a 4 nm thick silica layer on Si before any CO treatment. The incident photon energy is 700 eV.

immediately be observed, especially for intermediate binding energies between SiO_2 and Si bulk components. Indeed, least square fitting procedure leads to a peak deconvolution with 4 components: A and B corresponding to silica and Si substrate and 2 additional C_1 and C_2 components at 2.5 and 1.7 eV of binding energy relative to the bulk. The decompositions for different photon energies are in excellent agreement, only the relative intensity of the peak is varying when the energy is changed. These intensity variations will be discussed later. A first observation can be made about A and B components: the intensity of SiO_2 component is now higher than the intensity of Si bulk whereas it was lower for the sample before CO treatment (Fig. 1), although the photon energy used for data presented on Fig. 1 is lower (and thus more surface sensitive) than the one used for data shown in Fig. 2. This gives an evidence that CO treatment leads to extra growth of silica.

We now focus on the additional components, C_1 and C_2, which appeared after the annealing under CO. The binding energy obtained for component C_1 is in agreement with silicon oxicarbide formation, more likely SiO_2C_2 [16]. On the other hand C_2 component can be attributed either to SiC or $SiOC_3$. Actually, C_2 component can be assigned to SiC formation as will be shown with C1s core level spectra. For C1s core-level spectra (Fig. 3), least square fitting was performed using Voigt function with 100 meV Lorentzian width. The decomposition involves 3 components D_1, D_2 and D_3 at respectively 284.2, 283.6 and 282.8 eV of binding energies. This decomposition is valid for all photon energies used (Fig. 3). We can notice that when the photon energy decreases, the relative intensity of D_2 component strongly increases whereas D_1 and D_3 peak intensities decrease. This shows that D_2 peak can be attributed to carbon at the surface of the sample, most likely corresponding to C–C bonds. The other components can be attributed to oxycarbide and/or silicon carbide. Actually, the existence of 2 components D_1 and D_3 assures that we have silicon carbide as well as oxycarbide. Indeed oxycarbide corresponds to a carbon atom bounded to an oxygen and a silicon atoms, this means the C1s level energy will not change so much for different kinds of oxycarbide [17]. If we only had SiO_2C_2 and $SiOC_3$ then we would get only one component in the C1s spectra. In our case, the D_3 component is attributed to SiC formation, in agreement with what is observed on the Si2p spectrum. Its binding energy is 282.8 eV, in agreement with previous results [18]. But as pointed out by Dufour et al., the values of C1s binding energy in SiC reported in the literature are quite spread due to difference in band bending from one sample to another [19]. In this paper the authors show that the binding energy difference between Si2p and C1s components corresponding to SiC is much more representative of the real nature of the chemical bonding between Si and C. In our case, this energy difference is $\Delta = 182.1$ eV. This is