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Structure determination of three-dimensional hafnium silicide nano structures on Si(100) by means of X-ray photoelectron diffraction

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A B S T R A C T

We propose a modified zirconium silicide model for the structure of $HfSi_2$ islands on Si(100). We studied this system in a combined investigation by means of photoelectron diffraction (XPD), photoelectron spectroscopy and atomic force microscopy. Synchrotron radiation was used for enhanced energy resolution and surface sensitivity. Calculated XPD patterns of model clusters reflecting the structure as well as the morphology of the islands exhibit an excellent agreement with the experimental results. From LEED and AFM measurements a preferential nano structure growth along the [011] and $[0\bar{1}1]$ direction was observed. Complementary XPD results clearly show that the $HfSi_2$ structures are silicon terminated.
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1. Introduction

$HfSi_2$ has attracted recent interest in various fields in science. New materials are needed in the semiconductor industry in order to retain the design of MOSFET devices and to proceed in the ongoing miniaturization. The currently used SiO_2 gate dielectric becomes inefficient for ultrathin layers of this material [1] due to increasing tunneling currents through these films. Presently, several metal oxides are under investigation as a substitute for SiO_2 [2,3]. One of the most promising candidates is hafnium oxide which fulfills the basic requirements for the designated application [2]: these include a high dielectric constant ($k \approx 25$), a large bandgap ($\Delta E = 5.7$ eV), and a large band-offset to silicon ($\Delta E_{Si} = 1.5$ eV). Today, the major concern is the thermal stability of the system HfO_2/Si(100). During the last five years it was shown that annealing of the system at temperatures above 700 °C leads to the formation of three-dim metallic $HfSi_2$ structures, destroying the insulating properties of the dielectric film [4,5]. From the theory side, the formation of surface is simulated by calculations on enthalpies or by the introduction of surface stress, for example. For these simulations the internal $HfSi_2$ structure holds valuable information.

Among other silicides [6,7] $HfSi_2$ is under consideration to form self-assembled nano-structures of a high lateral aspect ratio upon annealing, mainly depending on the amount of hafnium present on the surface. Nano-structures with an aspect ratio of 70 were already reported by appropriate preparations [8]. Therefore, a detailed understanding of this system promises valuable information in order to control electronic and geometric properties of structures in the field of quasi one-dimensional nanowires. In particular, the study of nanowires on semiconductor surfaces has accumulated a sizeable literature [9,10]. In general, these studies have utilized a combination of scanning tunneling microscopy and theoretical calculations and did not involve structure determinations at the atomic scale. A reliable structural model is indispensable in order to estimate the electronic properties of these structures for applications in nanometer-sized wire connections of microelectronic devices.

In this report, we present a first structure determination of hafnium silicide nanowires on a semiconductor surface. We used a high-flux beamline tuned to energies for high surface sensitivity. We measured around 8000 spectra at various emission angles in order to cover the half space above the crystal, and applied a three-dimensional island model in the simulations including an *R*-factor analysis. Therefore, the results reflect the surface sensitivity and data base completeness required for surface structure determinations using XPD [11]. These characteristics were not shared by a previous XPD study on Bi nanowires on Si(100) applying Mg Kα radiation and a data set recorded at a constant

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polar angle [12], which conclusions were questioned [9,10,13]. Here, we propose a modified zirconium silicide structure for the silicide surface islands. We calculated photoelectron diffraction patterns using model clusters of atoms reflecting this structure as well as the morphology of the islands. A comparison with experimental XPD patterns and with real-space images of the islands recorded by atomic force microscopy leads to an unambiguous picture, which includes the influence of the Si substrate on lattice distortions for different film thicknesses. In this study, we show that XPD can be used to determinate nanometer sized island structures on surfaces.

2. Experiment

All experiments were carried out in an ultra-high vacuum chamber with a base pressure of 5×10^{-11} mbar. The Si(100) samples were cut out of a silicon wafer and cleaned in-situ by flash annealing at 1050 °C. The (2×1)-reconstruction of the clean Si surface was verified by LEED. XPS spectra were recorded to check for sample impurities. In a next step hafnium was evaporated onto the sample from a hafnium wire by electron beam evaporation. The samples were kept at room temperature during this process. Further experimental details can be found elsewhere [14]. The film thickness was estimated from the signal strength of the Si 2p photoelectron yield attenuated by the initially amorphous hafnium film with an uncertainty of around 1 Å. All Hf-films on Si(100) were annealed at 750 °C for at least 10 min. The photoelectron diffraction patterns were recorded over a polar angle range of $6^{\circ} \leqslant \theta \leqslant 78^{\circ}$, and over a full 360° azimuthal range, in steps of 2° for both angles. In order to enhance surface sensitivity, we tuned the photon energy to $h\nu$ = 180 eV, with an energy resolution in this case is ΔE = 0.1 eV. The AFM measurements were performed in a separate UHV chamber. The samples for the AFM experiments were prepared according to the previous recipe. Surface periodicity and sample purity were checked with identical LEED and Auger systems in both experimental set-ups.

The photoemission data were processed by removing the background of the inelastic scattered electrons (Shirley-Background) [15]. The signals were decomposed using Gaussian and Doniach–Sunjic profiles to distinguish different chemical species on the surface [16]. The XPD patterns obtained from these signals were normalized to the synchrotron light intensity and were symmetrized according to the fourfold symmetry of the raw data to suppress random fluctuations. In particular, the symmetrization was carried out by averaging over the data for equivalent angle-pairs.

3. Results

Fig. 1a displays an overview spectrum obtained from the hafnium silicide surface after annealing at 750 °C. Except for the hafnium and silicon signals, no further elements or impurities are detectable within the sensitivity of XPS. Especially, the absence of an oxygen 2s photoelectron signal at a binding energy of around $E_{\rm bin}$ = 23 eV is important here, as it often appears in samples prepared by electron beam evaporation. The inset of Fig. 1a shows a high-resolution spectrum of the Hf 4f signal. The spectrum was decomposed into an asymmetric Doniach–Sunjic doublet separated by 1.7 eV, indicating the metallic character of the islands. The excellent fit to the experimental data shows that only one chemical component of Hf is present on the surface. Its Gaussian width was set to $w_{\rm G}$ = 0.8 eV, the Lorentzian width could be kept below $w_{\rm L}$ = 0.1 eV. The asymmetry turned out to be $\alpha \approx 0.13$. Similar results were found for other metallic compounds of hafnium [17]. By comparing the peak position of the known Si $2p_{3/2}$ bulk signal at $E_{\rm bin}$ = 99.2 eV to the position of the Hf $4f_{7/2}$ signal within

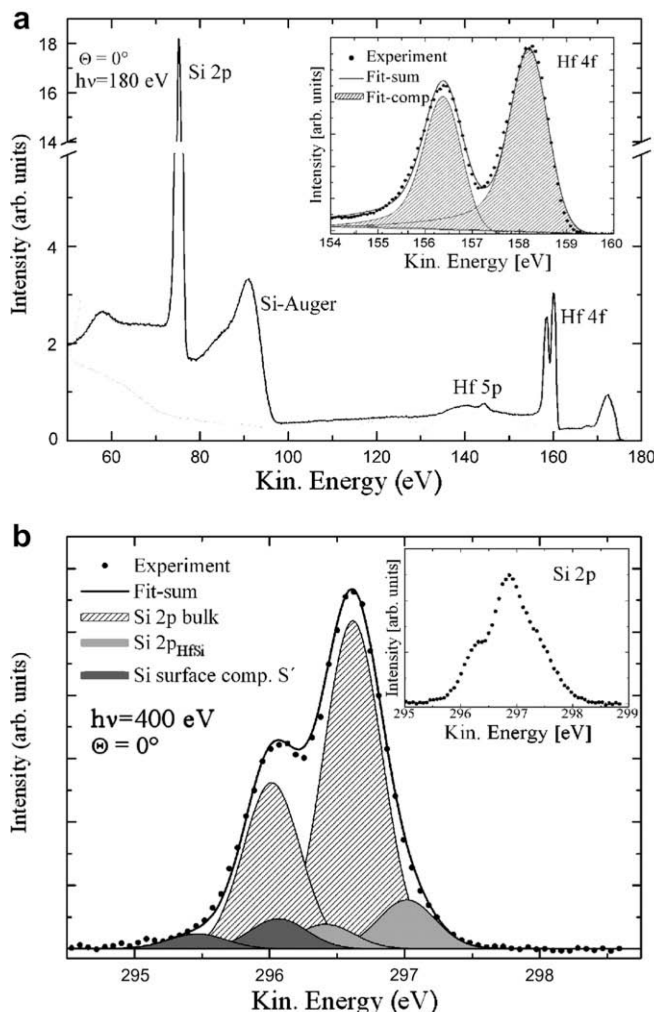

Fig. 1. XPS spectra of the investigated Hf/Si(100) films. Overview spectrum (a) and a high resolution spectrum of the Hf 4f signal (inset). The experimental data (black dots) can be approximated by a set of Doniach–Sunjic profiles. High-resolution XPS spectrum (b) of the Si 2p signal before (inset) and after annealing at 750 °C.

the $HfSi_2$ compound, the Hf $4f_{7/2}$ binding energy could be determined to be 14.7 ± 0.05 eV [18,19]. The binding energy of the pure Hf species is between 14.2 and 14.3 eV. The resulting shift of 0.4–0.5 eV was observed before. In the spectrum of the annealed samples (Fig. 1b), the dominant photoelectron intensity originates from Si bulk atoms (solid line, hatched), regardless the initial surface coverage; the inset in Fig. 1b represents the Si 2p signal of the sample before annealing. Additionally, the decomposed spectrum displays the $HfSi_2$ and the silicon surface S' [20] components with a shift of 0.35–0.4 eV and 0.4-0.45 eV towards higher and lower kinetic energy, respectively. The S' originates from the uppermost layer of the Si-substrate, and thus has a slightly different binding energy compared to the bulk material. The $HfSi_2$ photoelectron signal is small because of $HfSi_2$ island formation during annealing (cf. Fig. 1b).

An investigation of the ratio between the Hf 4f and Si 2p signals by angle-resolved photoelectron spectroscopy (ARPES) indicated the formation of islands on the surface. Since this method cannot provide a clear model of the surface morphology, we investigated the reported island formation of $HfSi_2$ on Si(100) [8,21] and its formation under our preparation conditions by complementary AFM measurements. Fig. 2a displays a $400 \times 500\,\rm nm^2$ AFM image of the sample surface after annealing at 700 °C. The orientation of

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