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Evolution of chemical states within the HfO_2/Si(100) interface upon annealing, prepared by direct electron beam evaporation

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ABSTRACT

We demonstrate the preparation of the system HfO_2/Si(100) by direct evaporation of hafnium dioxide from a specially prepared electron beam evaporator. Investigating the system by means of photoelectron spectroscopy in the soft X-ray regime, we show the system's interface being free of silicon dioxide and hafnium silicide after evaporation. Upon annealing the formation of SiO_2 at the interface is investigated by using high resolution photoemission spectra. Their separation into different sub-oxides at the interface is presented. The structural order at the crystalline/amorphous interface is investigated by X-ray photoelectron diffraction. The system's degradation is observed at above 700 °C.

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1. Introduction

Ultra-thin hafnium dioxide layers are candidates for forming advanced gate dielectric for field effect transistors, along with other transition-metal oxides and rare-earth oxides. They ought to replace SiO_2 as a gate dielectric, due to favorable electronic properties, having in particular a significantly higher dielectric constant κ compared to silicon [1,2]. Presently, their use is thought to be one of the solutions proposed to keep up the miniaturization process in the semiconductor industry, although, their thermal stability is questionable [3–5]. Tempering the layer stack at temperatures up to 1000 °C is an inevitable part of the active production process of metal-oxide field effect transistors (MOSFETs) and cannot, so far, be omitted. This process leads to partial or full silicidation of hafnium, destroying the system's insulating properties. Ultra-thin layers of HfO_2 and other, so called, high-k dielectrics are usually applied to the surface by atomic layer deposition (ALD), or chemical vapor deposition (VCD). A variety of publications in different fields of the surface science community deals with these sophisticated methods [6–10]. Furthermore most of the characterizations are performed by AFM and STM.

In or present work we prepared the HfO_2/Si(100) system by evaporating monolayer thin layers of HfO_2 directly onto the substrate via electron beam evaporation (EBE). Literature reporting EBE usually refers to an evaporation of metallic hafnium onto the silicon surface followed by annealing in an oxygen ambient atmosphere [3]. As a result, we demonstrate the formation of a SiO_2 as well as a $HfSi_2$ free interface by following the evolution of the system by XPS and XPD. Changes at the interface due to annealing can be clearly identified by the growth of a SiO_2 layer, not a hafnium silicate layer, already at temperatures below 500 °C. We show that the interface is much less ordered than for thermally grown silicon dioxide films. We report the system's degradation at a temperature of 700 °C.

2. Experiment

The experiments were carried out in-situ in an ultra-high vacuum chamber with a base pressure of 5×10^{-11} mbar. Si(100) samples (p-doped) were cut of an industrial wafer and cleaned in iso-propanol. The native oxide layer was removed by flash annealing to 1000 °C inside the vacuum chamber. Afterwards, the (2×1) surface reconstruction was formed by gradual cooling. The reconstruction was finally checked by low energy electron diffraction (LEED) and XPD patterns that were recorded and referenced to diffraction results obtained in previous silicon investigations. Hafnium oxide was evaporated onto the samples using an electron beam evaporator equipped with a special holding mechanism to carry grains of HfO_2. It consists of twisted tungsten wires ending in a cage for the oxide. To omit the evaporation of impurities, cage and oxide were degassed in UHV for at least one day. After the evaporation, the silicon samples were subsequently annealed at different temperatures for 10 min. To omit broadening or shifts of the photoemission signals, a cooling period of half an hour was allowed after each the annealing cycles.

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XPS investigations were performed using an undulator beamline at the synchrotron-radiation facility DELTA in Dortmund, Germany (Beamline 11). To enhance the surface sensitivity of the experiments, photons having an energy of $h\nu = 200$ eV were used for excitation. Photoelectron diffraction patterns were recorded using the same excitation energy. A sample manipulator, designed for this purpose, allowed to record XPD patterns within a $2^\circ \times 2^\circ$ angular grid covering almost the complete half-space above the sample. Observation angles up to $\theta = 76^\circ$ were measured, were θ denotes the observation angle with respect to the samples' surface normal. For the azimuthal angle ϕ full circles were scanned, each containing 180 spectra. Around 7000 spectra were recorded by this method to obtain a full XPD pattern. Their angular depending intensity modulations, i.e. the diffraction effects, were transferred to a linear gray-scale and were projected back to the surface plane.

The HfO_2 layer thicknesses were calculated by the damping of the silicon bulk signal due to the HfO_2 overlayer. Assuming a closed layer directly after the evaporation, the XPD data were used in terms of an angle resolved photoemission spectroscopy study (ARPES) to determine the layer thicknesses. The layer thicknesses ranged from 5 Å and 10 Å.

3. Results

The most intense photoemission lines at this energy, i.e. the silicon 2p signal and the hafnium 4f signal, were chosen for the investigation. Fig. 1 displays the spectra obtained for the relevant elements hafnium and silicon directly after the evaporation. The experimental results are indicated by dotted curves. The Hf 4f signal was found to have a binding energy of around $E_{Bin} = (17.7 \pm 0.1)$ eV for the oxidized species. The Si 2p signal's binding energy was $E_{Bin} = (99.2 \pm 0.05)$ eV, for the silicon bulk signal. The uncertainty margins correspond to the experimental energy increment. All XPS spectra were normalized by the incident intensity. The background of secondary electrons was removed by subtracting the Shirley-background [11]. Levenberg–Marquardt and Simplex methods were used as fitting routines.

In the displayed spectra one observes the absence of silicon oxide and $HfSi_2$. This result was initially suspected in a preliminary investigation [12] and is now evident in the decomposition of the spectra. Silicon dioxide usually equals a 4+ oxidation of silicon. Its expected energy position [13] is marked in Fig. 1a. Its chemical shift is expected to be 3.6–4.2 eV depending on the layer thickness and also on the preparation method used. The layer thickness influences the shift by changes in the band-offset and screening by the silicon substrate for ultra-thin layers. The preparation method influences density, possible crystallization, and incorporated impurities, all having impact on the relative binding energy with respect to the silicon bulk signal.

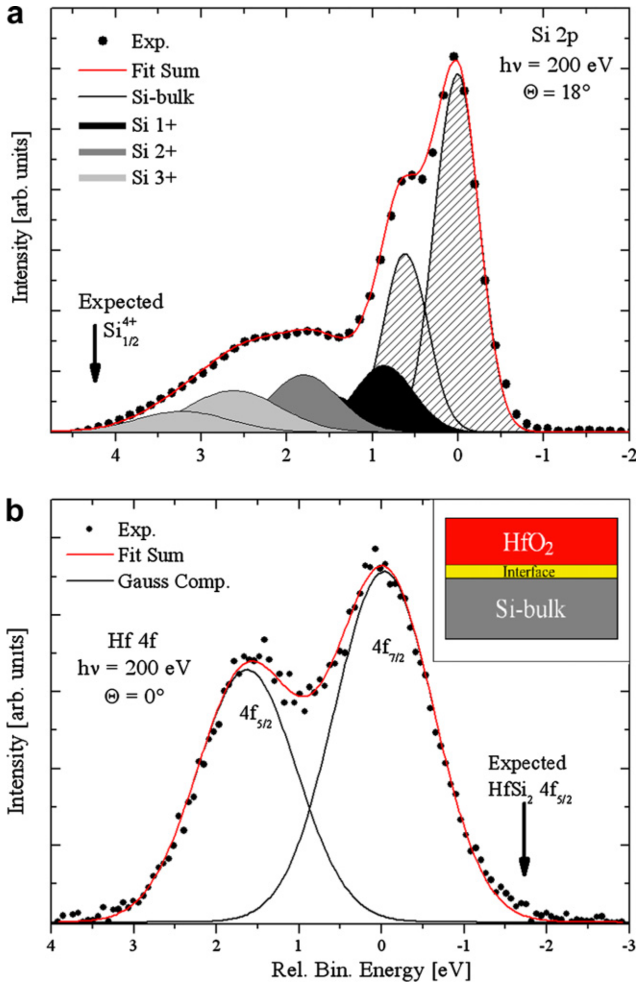

Fig. 1. XPS spectra of the investigated photoelectron signals. Silicon 2p spectrum (a) and Hf 4f spectrum (b). The experimental data (black dots) can be approximated by a set of Gaussian profiles (see text). The inset of (b) illustrates the system's layer stack directly after the evaporation of HfO_2.

Additional components appearing in the Si 2p spectrum besides the Si^0 component are expected to be caused by bonds with either oxygen or hafnium at the interface. This interface between the silicon substrate and the HfO_2 overlayer is illustrated in the inset of Fig. 1b. The position where the $HfSi_2$ photoelectron intensity is expected to appear is marked in Fig. 1b, exemplary the position for the $4f_{5/2}$-signal is denoted. The $4f_{7/2}$-signal would appear with a shift of 1.7 eV to higher kinetic energies with respect to the $4f_{5/2}$-signal. Relying to preceding investigations the energy position of hafnium silicide is about 14.1–14.3 eV [14,5], thus it is expected to appear shifted by $\Delta E = 3.3$–3.6 eV with respect to the main line. Here, no sub-oxide components are visible between the indicated silicide position and the HfO_2 main peak. A small intensity contribution appears at a relative binding energy of $E_{Bin} = -1.5$ eV. We allocate it to an increased number of dangling bonds. They could be repeatedly removed by annealing and vanished already at temperatures of 170 °C. The Hf 4f intensity appears to be broadened compared to spectra obtained from the 4f signal within $HfSi_2$ layers, indicating the presence of several slightly different HfO_2 modifications, denoting an amorphous layer. Its quasi-continuum of states cannot be resolved by the experiment. The signal's decomposition into a single Gaussian doublet shows the absence of Hf sub-oxides as well as $HfSi_2$. The doublet's intensity ratio was preset to 3:4, its energy separation to $\Delta E = 1.7$ eV. The expected intensity ratio can directly be derived from the jj-coupling in quantum mechanics. Good results were obtained for a peak width of $w_{Hf} = 0.60$ eV. This finding may point to the fact that HfO_2 bonds to the surface are intermediated by oxygen, leading to sub-oxide features in the silicon spectrum. Hafnium being the second next neighbor to silicon is also reported in the literature [15,16]. For proving this presumption the Si 2p spectrum was decomposed into different chemical components using a parameter set reported for the interface of the system SiO_2/Si(100) [13,18,17] using Gaussian line-shapes. The results are displayed beneath the experimental findings in Fig. 1a. Attention should be drawn to the number of free variables used. It should be as low as possible to allow unique conclusions regarding the interface chemistry. First, the eight peaks shown are not independent of each other, but forming four doublets, as indicated by same colors. Their shift with respect to each other and the $Si_{5/2}/Si_{3/2}$ intensity ratio were set to $\Delta E = 0.6$ eV and

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