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Temperature Dependent Defect Formation and Charging of Hafnium Oxides and Hafnium Silicates

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Abstract

Annealing of hafnium oxides and silicates, deposited on a thin SiON interlayer oxide grown on lightly doped Si (100) substrates, reveals an abrupt onset of charging at elevated temperatures. Photoexcitation of the substrate silicon below the dielectric stack using 30 femtosecond pulses of 400 nm light induces a photovoltage shift which can be accurately measured with photoelectron spectroscopy. The formation of trap states and the onset of charge injection at elevated temperatures are correlated with observed changes in the hafnium oxide layer including crystallization and surface roughening and disruption of the SiON interfacial layer.

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It has become abundantly clear that continued scaling of Si based CMOS devices requires the replacement of the traditional and highly successful SiO_2 gate insulator in favor of a material with a substantially higher dielectric constant. Hafnium oxides, silicates and variations thereof have been identified as potential contenders to replace silicon oxides, but have not yet achieved similar performance due, in great part, to defects which trap charge, impact carrier mobility and introduce threshold voltage variations.[1,2] A number of approaches by other workers have been employed to study the dependence of trap creation on growth[3,4], annealing conditions[5-7], and electrical stress[8].

In this letter we describe our investigations of the temperature dependent negative charging of hafnium oxides and silicates grown on thin SiON interlayers deposited on lightly doped n- and p- type Si (100) substrates. We employed a laser based source to carry out pump-probe photoelectron spectroscopy on samples during various stages of oxide growth and annealing. In these experiments, a 30 femtosecond (fs) amplified Ti:sapphire laser produces 1 mJ, 800 nm pulses at a repetition rate of 1 kHz. A fraction of this light is frequency doubled to 400 nm (3.1 eV) and is directed onto the sample. Near the Si surface the electronic band structure bends upward or downward in the presence of charged surface or interface states, or charge residing the dielectric deposited on the Si. Figure 1 displays an example for HfO_2 grown atop n-type Si (100). The main spectral features consist of the Hf 5d peak at –6 eV binding energy and the O2p at –9 eV. Also shown is a spectrum of thick Hf metal revealing the location of the Fermi level. Photoexcitation of the Si substrate with pulses of 400 nm photons generates up to ~$8X10^{18}$ e-h pairs/cm^3 in the Si depletion layer. Rapid rearrangement of these carriers in

response to the existing dipole field produces an equal and opposite field which flattens the bands. By employing photoelectron spectroscopy to monitor the electronic structure of both the excited and the unexcited sample, the magnitude and direction of the band bending can be accurately determined.

All spectra in our experiments were collected with 26.35 eV probe photons, generated by focusing pulses of 800 nm light into a bursts of Ar gas near the front end of an evacuated beam line connected to our ultrahigh vacuum (UHV) system. High order, odd multiple harmonics are generated and an individual harmonic, in our case the 17^{th} at 26.35 eV, is selected by a toroidal diffraction grating and refocused onto the sample at the same spot irradiated by the 400 nm (pump) light. An optical delay line assures temporal overlap of the pump and probe pulses. Details of the fs photoelectron spectroscopy system are given elsewhere.[9]

HfO_2 layers were grown either in-situ in our (UHV) (base pressure $2X10^{-10}$ torr) or ex-situ in a CVD growth system. $HfSiO_2$ layers were grown in the external CVD system. For in-situ grown HfO_2, Si substrates with a thermally grown SiON interlayer (~1 nm) were first degassed at 700 C for 2 minutes. Experiments on SiO_2 interlayers were also carried out and will be described elsewhere. Metal oxide growth proceeded by exposing the Si substrate to a flux of evaporated Hf during immersion in an O_2 ambient ($P=1X10^{-5}$ torr) at room temperature (RT).[10] The metal deposition rate was monitored in-situ with a quartz crystal monitor cross-calibrated with Rutherford Back Scattering. The CVD samples were grown at 500 C, transferred in air to our UHV system and degassed in vacuum.

Once the dielectric stack was grown, both unexcited and photoexcited spectra were collected after the sample was annealed at a specific temperature and then allowed to cool to near RT.

Figure 2a displays a series of measurements on p-type ($p\sim1X10^{15}/cm^3$) Si (100) with a dielectric stack consisting of 1 nm SiON and 1.2 nm HfO_2. The band bending values for temperatures ranging from RT to 800 C are plotted together with the oxide charge. With increasing temperature, the value of the band bending decreases up to ~600 C, followed by a precipitous drop through 700 C into accumulation, wherein the bands (normally bent downward for p-type) are bent upward. Such behavior indicates that negative charge is driven into states in the dielectric stack. Also shown in Fig. 2a are data (open circles) from SiON on Si(100) without HfO_2 . Unlike the HfO_2 covered system, the bands shift only 150 meV out to 900 C, indicating the changes we observe occur predominantly in the HfO_2 layer.

Figure 2b shows the analagous series for n-type ($n\sim4X10^{14}/cm^3$) Si(100) with a dielectric stack consisting of 1 nm SiON and 1.5 nm HfO_2. We note here virtually no change in the band bending up to a temperature of ~700 C beyond which we observe an abrupt change. Also plotted is a series of measurements for $HfSiO_2$, grown ex-situ by CVD, which shows similar behavior except that the abrupt change occurs at ~100 C higher temperature. $HfSiO_2$ has been observed to crystallize at a higher temperature than HfO_2[11,12], a result which suggests, as we will discuss, that crystallization plays a role in the onset of the observed film charging with temperature.

Common to both n- and p-type substrates, and for a wide range of samples we investigated, is the abrupt and substantial change in the band bending at temperatures above 700 C, induced by negative charging of the dielectric stack. The amount of charge injected into the oxide can be calculated from the magnitude of band bending at each temperature and is given by:[13]

$$Q_{SCR} = \pm \frac{kT}{e} \varepsilon\varepsilon_o \frac{\sqrt{2}}{L} \sqrt{\frac{\cosh(u_b) - v(0)}{\cosh(u_b)} - v(0)\tanh(u_b) - 1}$$

Where L is Debye length, $u(z) = \frac{(E_F - E_i(z))}{kT}, v(z) = u_b - u(z)$, and u_b is bulk value of u(z). The results of these calculations are shown in Fig 2a and 2b. For p type samples, negative charge density of $6X10^{11}/cm^2$ is observed.

To test the stability of the trapped charge in the HfO_2 films, the samples were annealed up to 700 C in UHV, cooled and remeasured. No change in the band bending was observed. In addition, samples left in the UHV system overnight and measured again, 16 hours later, revealed no change in the band bending; both experiments indicate that the injected charge is highly stable. In a separate experiment, the reversibility of the charging was investigated by exposing an n-type sample to 1 $X10^{-5}$ torr O_2. Results are displayed in Fig. 3. Before exposure a band bending of 550 meV was measured, which reduced to 200 meV until temperatures in excess of 700 C were attained. Above 700 C the band bending returned to a value of 550 meV indicating that the defects originally created were

passivated. While the detailed nature of the defects is uncertain, dangling bonds as well as oxygen vacancies would be affected by the introduction of oxygen.

To investigate the relationship between the onset of charging and structural changes in the Hf oxide and silicate films, TEM was performed on 2.8 nm thick films, grown on 1 nm SiON interlayers, annealed at temperatures below (600 C) and above (820 C) the charging onset. At 600 C, the film shows a mostly amorphous character with sparse evidence of crystallite formation, while at 820 C a higher density of crystal grains is observed. Also at 820 C the SiON layer is disrupted, the HfO_2 layer is broadened and the surface is roughened. We also note a sharpening of the Hf 5d and O 2p peaks at 820 C.

These results suggest a correlation of trap formation with conversion of the amorphous layer to polycrystalline in addition to evidence of interlayer oxide disruption and diffusion. Simple tunneling calculations, carried out for our experimental conditions indicate that during annealing, thermally generated carriers, approaching $1X10^{18}/cm^3$, can tunnel into the Hf oxide/silicate layers where they are subsequently trapped. Since the conduction band offset between Si and SiON is ~ 1eV smaller than the valence offset, electron tunneling is favored[14]. While our observations reveal electron trapping and the correlations with morphological changes, the detailed identification of the traps is difficult. Defects in the form of dangling bonds at grain boundaries of polycrystalline HfO_2 can provide a source of states which firmly trap charge. Although no significant changes of photoelectron signal in the region from 0 to –3eV binding energy were observed for temperatures at or below 850 C, the TEM micrographs clearly show

disruption of oxide interfaces, indicating generation and diffusion of defects, most likely oxygen and oxygen vacancies which can trap tunneling electrons.[15] Polycrystalline grain boundaries in the HfO_2 film may assist in the charging process by providing an efficient diffusion path, consistent with the temperature dependent charging we observe. Well above the charging onset temperature however, spectral features extending to the Fermi level were observed whose shape and intensity were consistent with recently reported Hf_2Si formation.[16-19] Independent of the detailed nature of the traps, the experiments described in this letter provide direct evidence of charge injection into hafnium oxides and silicates which may significantly impact the performance of devices processed at elevated temperatures.

In conclusion, we have observed the abrupt negative charging of Hf oxide and silicate films at elevated temperatures using pump-probe photoelectron spectroscopy. We found that crystallization of the oxide film and interfacial reactions were correlated with an abrupt onset of negative charging. Possible mechanisms were described based on the experimental results.

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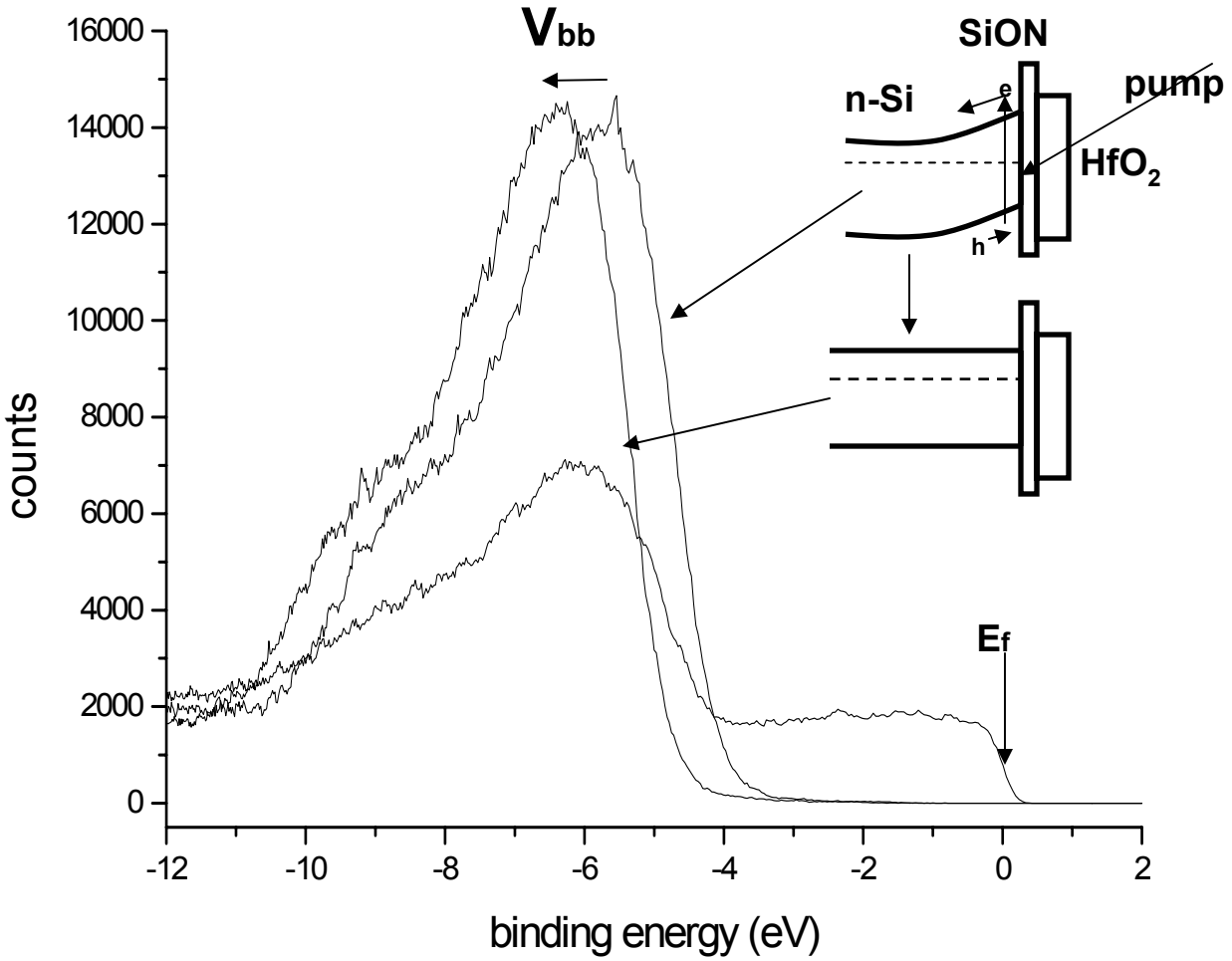

Fig. 1. Photoelectron spectra collected from unpumped and pumped HfO_2. The inset displays the process of photoexcitation of n-type Si covered with a SiON interlayer and HfO_2. Under photoexcitation electrons and holes excited in the Si substrate rearrange, resulting in flattening of the Si bands and a resultant shift in the photoemitted spectrum. Also shown is a spectrum collected from a thick Hf metal layer used to identify the Fermi level, E_f.

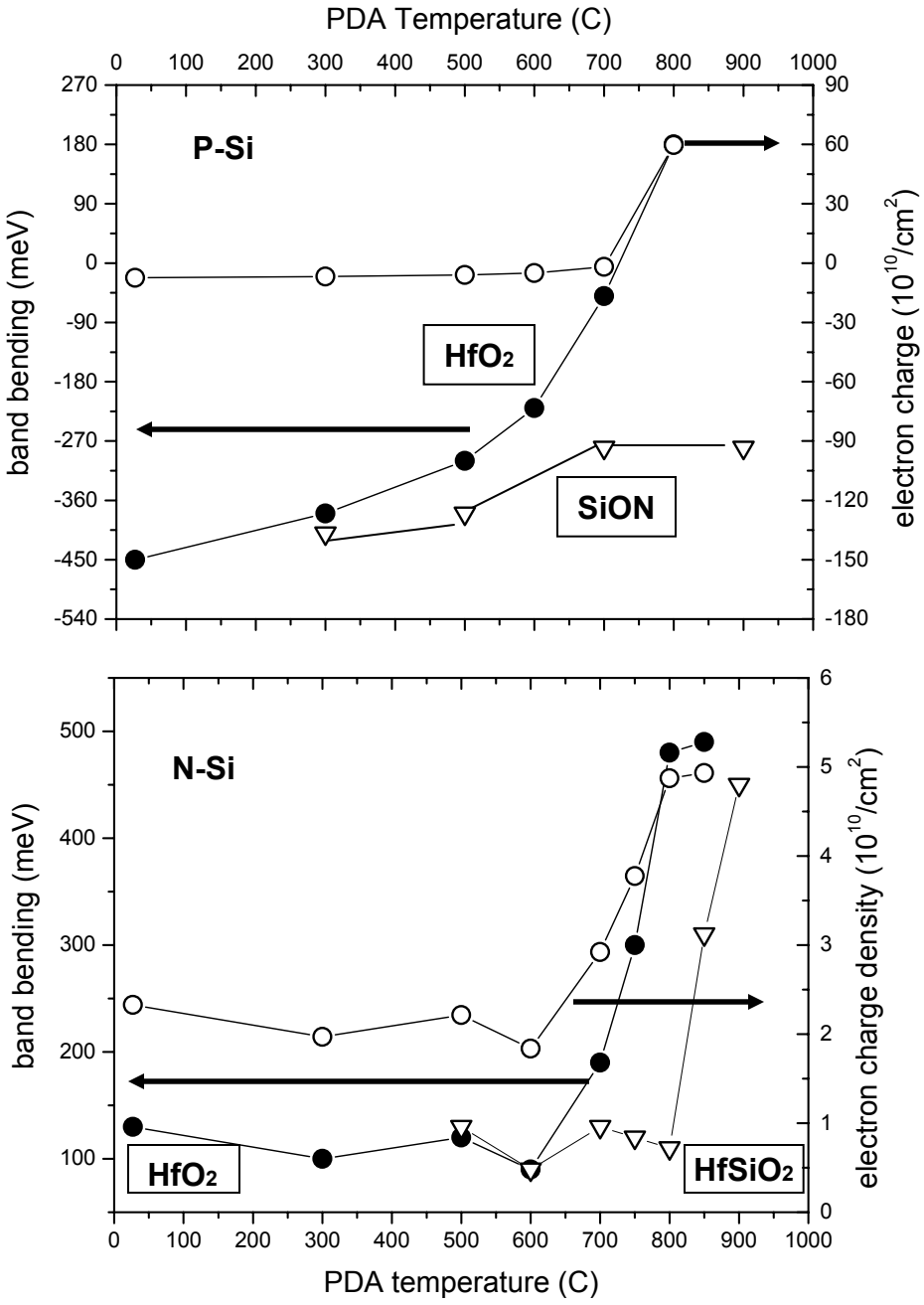

Fig. 2

a) **Band bending as a function of post-deposition-anneal temperature for HfO_2 (solid circles) and SiON (open triangles) on P-Si(100). Also shown is the charge (open circles) resident in the HfO_2 layer calculated from the magnitude of the band bending, whose scale is on the right.**

b) **Band bending as a function of post-deposition-anneal temperature for HfO_2 (solid circles) and $HfSiO_2$ (open triangles) on N-Si(100). Also shown is the charge (open circles) as described above.**

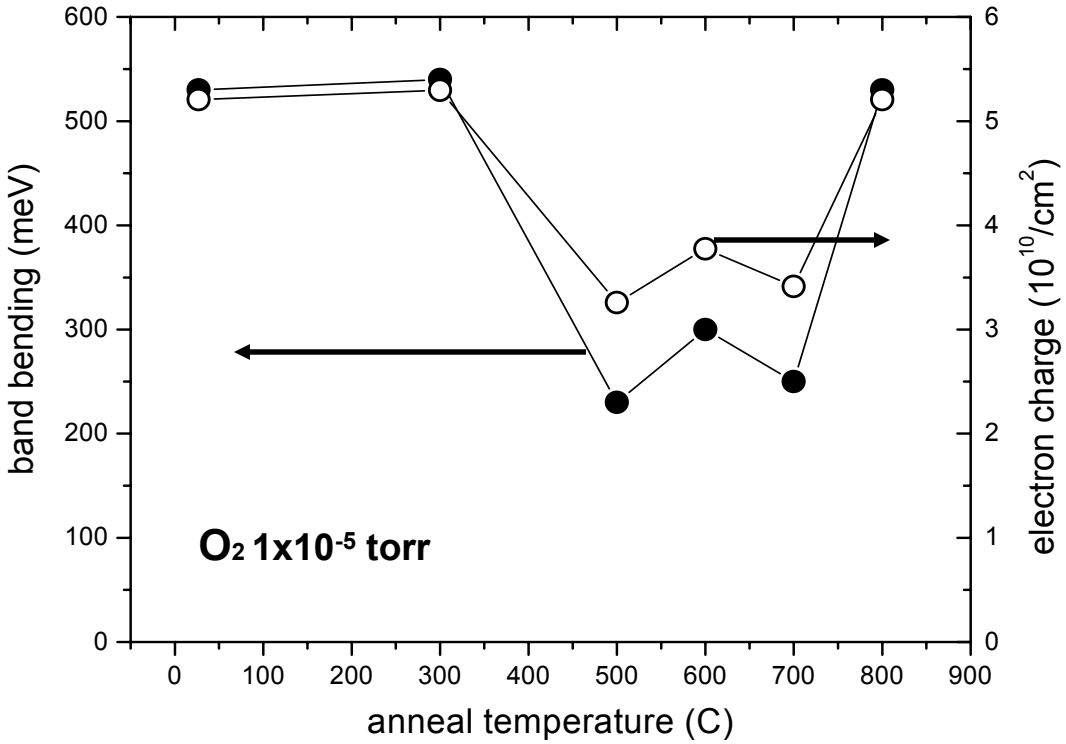

Fig. 3. Changes in band bending of HfO_2 (solid circles) exposed to 1X10^{-5} torr O_2 as a function of anneal temperature. The charge (open circles) resident in the HfO_2 layer is also shown.

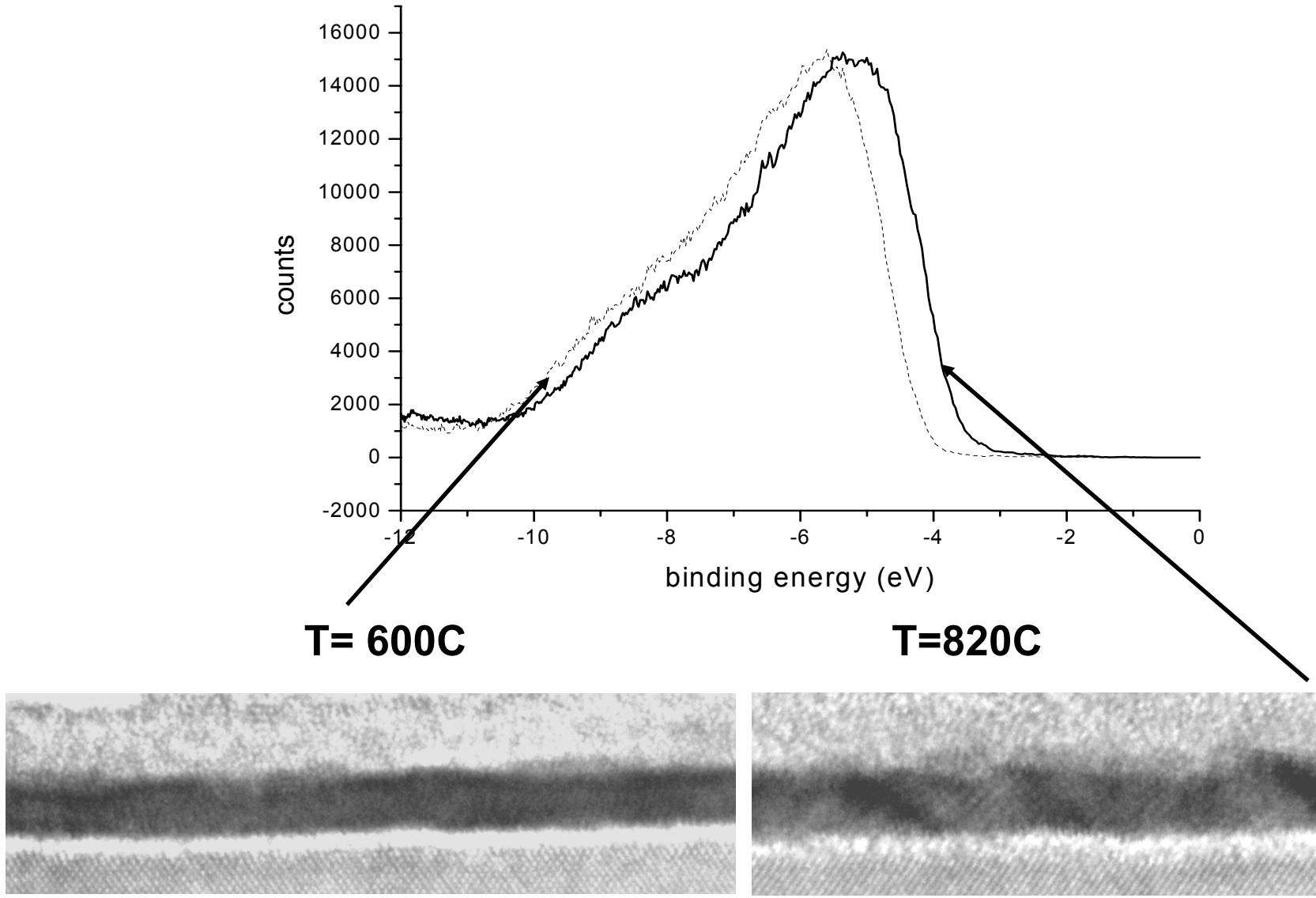

Fig. 4. TEM micrographs of 2.8 nm HfO_2 films grown on 1 nm SiON interlayers on Si (100) annealed at 600 C (left) and 820 C (right). Top spectra show a comparison of spectra obtained from the samples revealing a sharpening of the O_{2p} and Hf_{5d} features after annealing at 820 C.