Soft x-ray photoemission studies of Hf oxidation

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Soft x-ray photoemission spectroscopy has been applied to determine the binding energy shifts and the valance band offset of HfO_2 grown on Hf metal. Charging of oxide films upon x-ray exposure is found to be very severe and special care is taken to eliminate it. Photoemission results show the presence of metallic Hf (from the substrate) with a $4f_{7/2}$ binding energy of 14.22 eV, fully oxidized Hf (from HfO_2) with a $4f_{7/2}$ binding energy of 18.16 eV, and at least one clearly defined suboxide peak. The position of the valence band of HfO_2 with respect to the Hf(metal) Fermi level is 4.23 eV. © *2003 American Vacuum Society.* [DOI: 10.1116/1.1525816]

I. INTRODUCTION

Although photoelectron spectroscopy is widely used for elucidating the electronic structure of numerous materials, interfaces, and surfaces, systematic studies of hafnium and its oxides are scarce.[1–3] Sarma *et al.* employed x-ray photoelectron spectroscopy (XPS) to investigate oxides of second- and third-row transition metals, including those of rare earths.[1] They described the spin-orbit splittings and the binding energies of core levels of the metals. Specific features of individual oxides concerning satellites, multiplet structure, configuration mixing, and other properties were also discussed and binding energies of 29.8 and 16.4 eV were assigned to the $5p_{3/2}$ and $4f_{7/2}$ levels of HfO_2, respectively, Nyholm *et al.* reported the binding energies of all core levels in the N and O shells for the elements from hafnium to bismuth (that are accessible with Al $K\alpha$ radiation) using x-ray photoelectron spectroscopy.[2] They reported binding energies of 29.9 and 14.2 eV for the metallic $5p_{3/2}$ and $4f_{7/2}$ levels of Hf as referenced to the Au $4f_{7/2}$ level (84.00 eV). The *Handbook of X-ray Photoelectron Spectroscopy* gives the binding energies of the Hf $4f_{7/2}$ as 14.4 and 16.7 eV for Hf(metal) and HfO_2, respectively.[3] Morant *et al.* were the first to report on a systematic XPS investigation of the initial stages of oxidation of hafnium.[4] They studied the oxidation kinetics of polycrystalline hafnium at room temperature under low oxygen pressures ($\sim 10^{-7}$ Torr) and reported that suboxides are formed in the early stages, and that HfO_2 formation proceeded through oxidation of suboxides. The film thickness saturates to a value of 12 Å (under their conditions) with an average Hf:O stoichiometry of 1:1.8. They

also reported 14.31 and 18.13 eV binding energies for the Hf $4f_{7/2}$ levels of the metallic Hf and HfO_2, respectively. As can be deduced from these studies, although the reported binding energies for Hf(metal) are in agreement with each other, those for the HfO_2 have a large scatter (as much as 1.7 eV).

Interest in hafnium dioxide has grown enormously since 1998 because of its promise for use as a high-*k* dielectric in future highly scaled memory and logic metal–oxide–semiconductor field effect transistor devices.[5–9] As a result, extensive use of XPS and other surface techniques have recently been reported on hafnium oxide and related systems.[6–8,10–12] Although HfO_2 has a moderately high dielectric constant and band gap (both useful for ultrathin dielectric applications in micro- or nano-electronics), charging during photon or electron irradiation can make it difficult to determine the binding energies and/or the chemical states accurately. This, in turn, may lead to incorrect assignments and conclusions. For example, the binding energy of the Hf $4f_{7/2}$ levels of a thick film HfO_2 can be estimated as 17.3 and 17.4 eV from the recently published data of Wilk *et al.* and Cosnier *et al.*, respectively,[6–8] again differing by about 1 eV from the previously reported values. Additional confusion may arise from incorrect assignment of the surface and the bulk states. Finally, we note that understanding the position of the valence band edges of oxides next to metals will become critical for future devices in which doped polysilicon is replaced by metal electrodes.

In this article, we present results from an investigation of the stepwise oxidation of polycrystalline hafnium foil using high-resolution (and surface sensitive) soft x-ray photoemission to accurately determine the binding energies, electronic states, and valence band offsets for the Hf/HfO_2 system.

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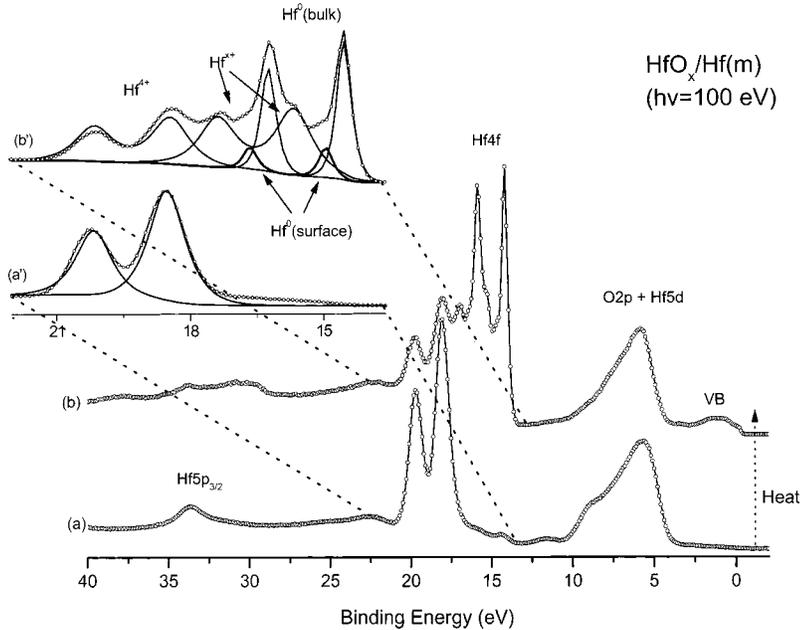
FIG. 1. Valence band, $4f$ and $5p$ photoemission spectrum of polycrystalline Hf foil recorded at 100 eV photon energy before [(a) and (a′)] and after [(b) and (b′)] *in situ* heating. The figure also contains the deconvoluted $4f$ region.

II. EXPERIMENT

Polycrystalline hafnium foil (0.025 mm thick) with a 3% Zr nominal content (Alfa Aesar) was used in this work. After cleaning with acetone and alcohol the foil was placed into the sample holder and loaded into the ultrahigh vacuum (UHV) chamber (base pressure 1×10^{-10} Torr) for *in situ* cleaning and controlled oxidation. Cleaning was accomplished in UHV by resistive heating of the foil. Controlled and stepwise oxidation was also accomplished in the UHV chamber by heating the foil to ca. 200 °C and exposing it to 1×10^{-5} Torr oxygen for various durations. Soft x-ray photoemission spectroscopy has been performed with monochromatic radiation at (i) the U8B beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory in the 120–400 eV range, and (ii) the 9.3 beamline of the Advanced Light Source (ALS) at Lawrence Berkeley Laboratory in the 70–400 eV range. We report our results to 10 meV accuracy for relative binding energies while the uncertainty in the absolute energy scale is slightly larger.

III. RESULTS AND DISCUSSION

The spectral features of the Hf foil immediately after introduction into UHV are presented in Fig. 1. The spectra clearly indicate the presence of a "native" oxide [Fig. (1a)] and only after *in situ* heating do features belonging to the metal emerge [Fig. 1(b)]. The deconvolution of the Hf4f spin-orbit couple is done after a Shirley background subtraction with the theoretical area ratio (3:4) held constant. The binding energy of the Hf $4f_{7/2}$ feature is reported as referenced to the Fermi energy of the cleaned hafnium foil. The Fermi energy is modeled by a Boltzmann broadened step function and the inflection point is found by fitting this function to the experimental data using a standard least-squares fitting method. As shown in Fig. 1(b′), the Hf4f region can

be fit to four spin-orbit doublets, each with 1.66 eV separation, with the corresponding $4f_{7/2}$ binding energies at 14.22, 14.58, 15.41, and 18.16 eV (see Table I). The first two doublets have relatively narrow linewidths ($\sim$0.4 eV) and can be assigned to the Hf^0 (bulk metal) and to the Hf^0 (surface metal). The energy separation between the $4f_{7/2}$ levels of the bulk and surface metal (surface core level shift) was 0.36 eV, in good agreement with single crystal[13] and polycrystalline[14] studies, the latter reporting a shift of 0.42 eV. The difference in core-level binding energies for the bulk and surface metal atoms results from a narrowing of the d bands at the surface; the narrowing requires a charge transfer to align the Fermi level. For transition metals with d bands less than half full such as Hf, the surface core levels are shifted to larger binding energies since the surface acquires positive charge.[15] The last two doublets exhibit larger widths ($>$0.9 eV) and can accordingly be assigned to a suboxide Hf^{x+}, and the fully oxidized hafnium Hf^{4+}. The 1.19 and 3.94 eV chemical shifts for the suboxide and the full oxide are in qualitative agreement with the previously reported XPS values of 0.90 and 3.64 eV respectively.[4] Similarly, the chemical shift in the binding energy of the Hf $5p_{3/2}$ level is determined as 3.9 eV exactly the same (within our experimental uncertainty) as the $4f_{7/2}$ shift.

TABLE I. Binding energies (in eV) together with their full width at half maximum (in eV) and assignments of the peaks of clean and oxidized polycrystalline Hf foil.

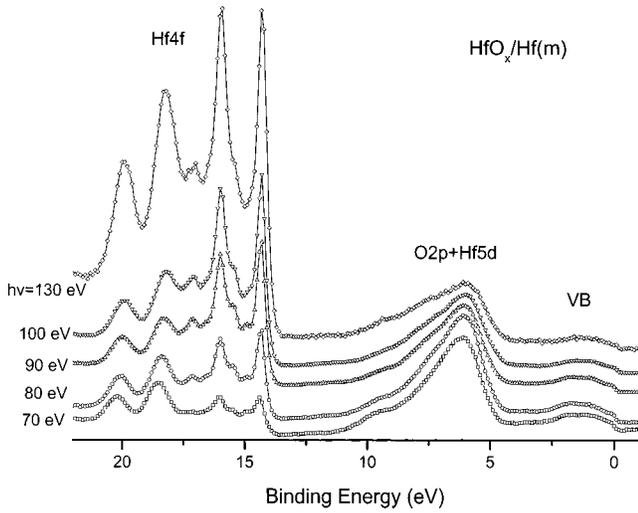|	VB onset (eV)	$4f_{7/2}$ (eV)	$5p_{3/2}$ (eV)
Hf^0 (metal, bulk)	0.00	14.22 (0.37)	29.9
Hf^0 (metal, surface)		14.58 (0.40)	
$Hf^{x+}O_y$ (suboxide)		15.41 (0.97)	
$Hf^{4+}O_2$	4.23	18.16 (0.92)	33.8

FIG. 2. Spectra of the VB and $4f$ region of the partially oxidized sample using different photon energies.

FIG. 3. Single scans of the Hf $4f$ region of a >20-nm-thick oxide sample recorded consecutively (a) and with a brief (ca. 10 s) anneal (without exposure to photon flux) between each scan.

Figure 2 presents the spectra of hafnium foil in the presence of the native oxide at different photon energies in the range of 70–130 eV. The use of synchrotron radiation with variable photon energy enables an assignment of the bands (for example, O $2p$ versus Hf $5d$, $6s$ midgap bands) as shown in Fig. 2. As the photon energy increases (increasing the escape depth of electrons), there is a decrease in intensity in the 0–4 eV range, indicating that the valence band of the metal is mainly composed of Hf $5d$ and $6s$ bands. The band in the range of 4.5–10 eV is mainly composed of O $2p$-like nonbonding π orbitals with some contribution from Hf $5d$ levels. It is worth noting that the shoulder at around ~7.5 eV becomes more pronounced with increasing photon energy.

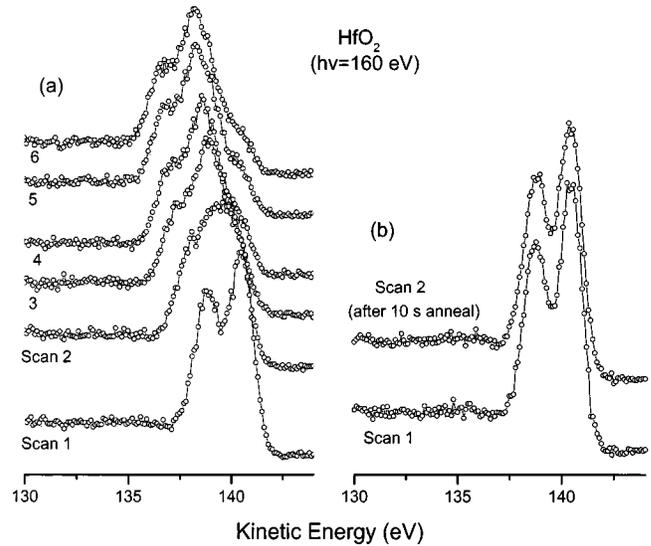When the thickness of the oxide layer is increased (>20 nm), the sample undergoes extensive charging result-

ing in a significant shift to lower kinetic (higher binding) energies, which varies with flux and/or time. Figure 3(a) shows the photon induced charging shifts that result when scans are taken consecutively at 2 min intervals. Under our conditions, we observed shifts on the order of 2 eV in the spectral features due to charging. The charging can, however, be eliminated even for these thick oxides by a 10 s brief anneal to ~200 °C (without exposure to photon flux) as shown in Fig. 3(b). Therefore special care should be paid when analyzing thicker oxides, as temporal and thermal changes in charging may confuse the analysis. Multiple recording of a single scan spectrum with annealing in between
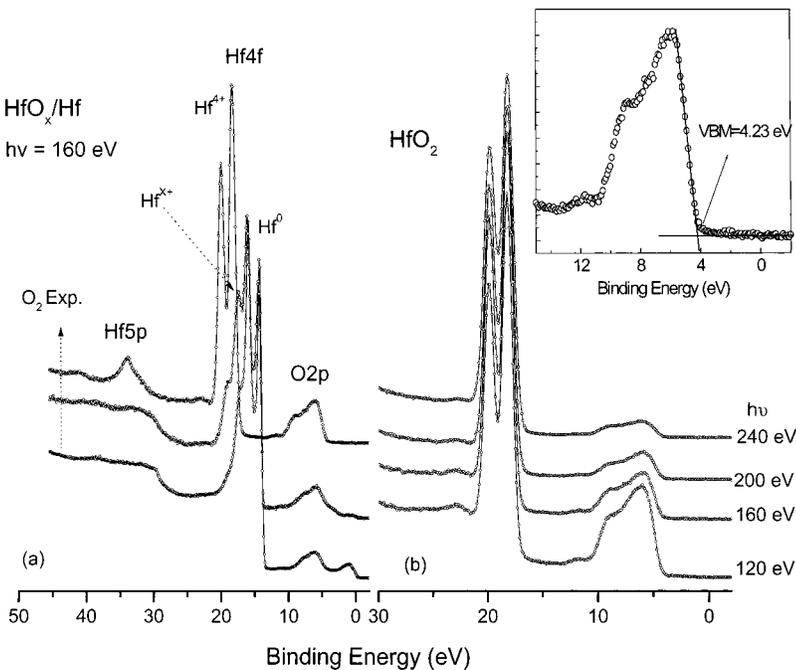

FIG. 4. Spectra recorded at 160 eV photon energy during the stepwise oxidation of the Hf foil (a), and of the fully oxidized sample at different photon energies (b). The inset shows the fitting of the valance band offset of the fully oxidized sample.

the scans (without photon exposure) is one way to minimize charging.

The spectra corresponding to different O_2 exposures are given in the left panel of Fig. 4. As the oxygen exposure increases, the intensity in the valence band region decreases (0–4 eV) and the band corresponding to O $2p$-like levels (4–10 eV) increases in intensity. The right panel presents the spectra of the fully oxidized sample in the energy range of 120–240 eV. This data set depicts the excitation energy dependence of the valence band cross section. The cross section of the valence band decreases as excitation energy increases as noted above. By sequentially oxidizing the sample, spectra can be obtained free from any charging effects. Hence stepwise and controlled oxidation is found to be a solution to accurately determine the chemical shift(s), valence-band offset(s), etc. of the oxide/metal system, as depicted in Fig. 4.

The position of the valence band maximum with respect to the Fermi level is determined using several different methods. We present a method that employs a best straight line fit to represent the decay in valence band photoemission and the point of intersection of this line with the baseline is taken to be the valence band edge. In the inset of Fig. 4, the result of the fitting is given, showing valence band offsets of 4.23 eV. This is the first report on the position of the valence band with respect to the Fermi level to the best of the authors' knowledge.

IV. CONCLUSION

Charging of oxide films under x rays (or other irradiation) is an important issue that must be taken into consideration for determination of core-level binding energies as well as valence band offsets. Measurements were taken as a function of time, thickness, and annealing condition. Photoemission results show the presence of metallic Hf (from the substrate) with the $4f_{7/2}$ binding energy of 14.22 eV, fully oxidized Hf (from HfO_2) with the $4f_{7/2}$ binding energy of 18.16 eV, and at least one clear suboxide peak. The Hf $5p_{3/2}$ chemical shift is exactly the same as that of $4f_{7/2}$. The position of the valence band of HfO_2 with respect to the Hf(m) Fermi level is determined as 4.23 eV.

[1] D. D. Sarma and C. N. R. Rao, J. Electron Spectrosc. Relat. Phenom. **20**, 25 (1980).
[2] R. Nyholm, A. Berndtsson, and N. Martensson, J. Phys. C **13**, L1091 (1980).
[3] C. D. Wagner *et al.*, *Handbook of X-ray Photoelectron Spectroscopy* (Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, MN, 1979).
[4] C. Morant, L. Galan, and J. M. Sanz, Surf. Interface Anal. **16**, 304 (1990).
[5] C. T. Hsu, Y. K. Su, and M. Yokoyama, Jpn. J. Appl. Phys., Part 1 **31**, 2501 (1992).
[6] G. D. Wilk and R. M. Wallace, Appl. Phys. Lett. **74**, 2854 (1999).
[7] G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **87**, 484 (2000).
[8] V. Cosnier, M. Olivier, G. Theret, and B. Andre, J. Vac. Sci. Technol. A **19**, 2267 (2001).
[9] A. I. Kingon, J. P. Maria, and S. K. Streiffer, Nature (London) **406**, 1032 (2000).
[10] S. Sayan, E. Garfunkel, and S. Suzer, J. Appl. Phys. **80**, 2135 (2002).
[11] M. Belyansky and M. Trenary, J. Vac. Sci. Technol. A **15**, 3065 (1997).
[12] H. Lee, S. Jeon, and H. Hwang, Appl. Phys. Lett. **79**, 2615 (2001).
[13] N. Martensson *et al.*, Phys. Rev. B **39**, 8181 (1989).
[14] R. Nyholm and J. Schmidt-May, J. Phys. C **17**, L113 (1984).
[15] W. F. Egelhoff, Jr., Surf. Sci. Rep. **6**, 253 (1987).