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Research Article

X-Ray Photoemission Study of the Oxidation of Hafnium

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Abstract

About 20 Å of hafnium were deposited on silicon substrates using the electron beam evaporation technique. Two types of samples were investigated. In one type, the substrate was kept at the ambient temperature. After the deposition, the substrate temperature was increased to 100, 200, and 300∘ C. In the other type, the substrate temperature was held fixed at some value during the deposition. For this type, the substrate temperatures used were 100, 200, 300, 400, 500, 550, and 600∘ C. The samples were characterized in situ by the technique of X-ray photoelectron spectroscopy. No trace of elemental hafnium is observed in the deposited overlayer. Also, there is no evidence of any chemical reactivity between the overlayer and the silicon substrate over the temperature range used. The hafnium overlayer shows a mixture of the dioxide and the suboxide. The ratio of the suboxide to dioxide is observed to be more in the first type of samples. The spectral data indicate that hafnium has a strong affinity for oxygen. The overlayer gets completely oxidized to form HfO2 at substrate temperature around 300∘ C for the first type of samples and at substrate temperature greater than 550∘ C for the second type.

1. Introduction

In the semiconductor industry, the success of metal-oxide-semiconductor structures depends largely on the "near perfect" SiO_2/Si interface. With the continued downscaling of complementary MOS (CMOS) devices, SiO_2 seems to have reached its limits. As the MOS devices are scaled down to the 65 nm technology mode (physical gate length equal to 45 nm), the thickness of the gate dielectric needs to be less than 2 nm [1, 2]. In this regime, the major concerns are related to dramatic increase in direct tunneling leakage current and reliability issues associated with the SiO_2 films [3]. The only alternative is to increase the dielectric constant of the gate dielectric. Hafnium dioxide (HfO_2) is emerging as a high κ dielectric substitute for SiO_2 because of its large band gap, high κ and good thermodynamic stability on Si [4], compatibility with complimentary metal oxide semiconductor processing, and good reliability [5].

Investigation of HfO_2-Si systems has been focused on the direct deposition of HfO_2 thin films on silicon substrate using different deposition techniques: atomic layer deposition [2, 6], chemical deposition [7], reactive dc magnetron sputtering [4, 8], chemical vapor deposition [9], and e-beam technique [10]. Very few studies have been performed involving evaporation of elemental hafnium. Xing et al. [11] have deposited elemental hafnium on silicon and investigated the Hf/Si interface. Suzer et al. [12] have studied the oxidation of elemental hafnium using soft X-ray photoemission spectroscopy (XPS). Morant et al. [13] have studied the initial oxidation of hafnium foil by XPS. It has been observed that hafnium suboxide is formed in addition to the hafnium dioxide [9, 12, 13].

The formation of the suboxide depends on the substrate temperature and the depositing conditions. To our knowledge, no systematic investigation on the formation of hafnium suboxide and hafnium dioxide as a function of depositing conditions has been carried out.

In this investigation, we have studied the formation of hafnium dioxide and hafnium suboxide as a function of the substrate temperature. The technique of XPS has been employed for in situ characterization of the samples. The formation of the suboxide and the dioxide has been compared in two types of samples. One type consists of depositing the hafnium film at room temperature followed by annealing. In the other type, the substrate was brought to the desired temperature before the deposition. The results show a systematic variation in the content of the suboxide and the dioxide in these samples. The formation of the dioxide and the suboxide indicates that hafnium has a strong affinity for oxygen.

2. Experiment

Hafnium wires (2 mm diameter) of 96.7% (Alfa Aesar, Mass, USA) were used in this work. The sample contained nominal 3% Zr as impurity according to the supplier. The silicon substrates (100; *p*-type) used in the present investigation were cleaned with HF to get rid of any native oxide that might be present on the surface. Hafnium films with estimated thickness of 20 Å were deposited on silicon substrates. The thickness of the deposited films was calibrated using a quartz crystal oscillator. The deposition was carried out by the electron beam technique. The EGN4 electron gun (Oxford Applied Research, Oxfordshire, UK) was used for the deposition. Four samples in the form of wires can be mounted onto this gun. The sample to be deposited can be selected by selecting the appropriate filament. Two types of samples were investigated. For one type (labeled as type A), the substrate was kept at the ambient temperature during the deposition. After the deposition, the temperature of the sample+overlayer was raised to the desired value and held at that temperature for 30 minutes. For this type, the substrate temperatures used were room temperature (as-deposited), 100, 200, and 300 °C. In the other type (labeled as type B), the substrate was brought to the desired temperature prior to the deposition. After the deposition, the sample was held at that temperature for 30 minutes. The substrate temperatures used for this type of samples were 100, 200, 300, 400, 500, 550, and 600 °C. The base pressure before deposition was high 10^{-9} torr and rose to low 10^{-8} torr during the deposition. The deposition chamber is connected to the analysis chamber. The overlayers were characterized in situ by XPS.

Physical Electronics PHI 5100 ESCA system was used in the present investigation. The magnesium anode (energy = 1253.6 eV) was used as the source of excitation. For calibration purposes, pure silver, gold, and copper samples were used. The Cu $2p_{3/2}$ and Au $4f_{7/2}$ lines were set to give a binding energy (BE) difference of 848.6 eV. This established the linearity of the BE scale. The Ag $3d_{5/2}$ line was set at 368.2 eV, the Cu $2p_{3/2}$ line at 932.6 eV, and the Au $4f_{7/2}$ line at 84.0 eV. The full width at half maximum (FWHM) of the Ag $3d_{5/2}$ peak was determined to be 1.8 eV which gives a measure of the resolution. The base pressure during analysis was $< 10^{-9}$ torr. The survey spectra were taken with pass energy of 89.45 eV, and the multiplex spectra were taken with 35.75 eV pass energy.

3. Results and Discussion

The multiplex spectra in the hafnium 4f and oxygen 1s regions were recorded in the samples. The hafnium 4s peak has a BE of ~537 eV and thus overlaps (see, e.g., [14]) with the oxygen 1s region (around 535 eV). The analyses were, therefore, confined to the Hf 4f region. In the spectra recorded for all the samples, a shoulder is observed on the low BE side of the main peak in the Hf 4f region. Investigation of the silicon 2p region did not show any significant changes in shape and binding energy. The shoulder, therefore, does not correspond to any chemical interaction between the deposited hafnium overlayer and the silicon substrate under the deposition conditions used in the present investigation.

Figure 1 shows the multiplex spectra in the Hf 4f region for type A samples for the various temperatures. The multiplex spectra recorded in oxygen 1s region in these samples are shown in Figure 2. The spectra represent the average of thirty runs taken to reduce the statistical noise and thus to improve the signal-to-noise ratio. The Hf 4f spectra have been normalized to have equal intensity at 12.0 eV, and the oxygen 1s spectra have been normalized to have equal intensity at 527.0 eV. The major peak in spectra has been aligned for comparison purposes. In Figure 2, a shoulder is observed on the high BE side of the main peak in the oxygen 1s region. This is due to the Hf 4s core peak. This confirmed by the fact that this shoulder exists even when the hafnium overlayer is completely oxidized (spectrum corresponding to 300 °C in Figure 2).

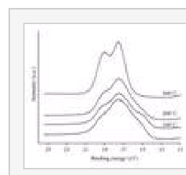

Figure 1: Normalized Hf 4f spectra in type A samples as a function of substrate temperature. The major peaks have been aligned.

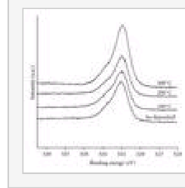

Figure 2: Normalized oxygen 1s spectra in type A samples as a function of substrate temperature. The major peaks have been aligned.

The BE difference between the Hf $4f_{7/2}$ levels in elemental Hf and in the dioxide has been determined to be 3.6 eV [12, 15]. Since BE difference between the main peak and the shoulder is less than this value (~1.7 eV), the spectra indicate no presence of metallic hafnium. The main peak is due to the formation of the hafnium dioxide as the elemental film gets deposited on the substrate. The presence of the shoulder is, therefore, interpreted as the formation of Hf suboxide. A slight increase in the intensity of the shoulder is observed as the temperature is increased to 200 °C. At temperatures higher than 200 °C, the intensity decreases and the shoulder is seen to disappear at a temperature of 300 °C. The spectrum of the sample at this temperature shows the presence of two peaks corresponding to the $4f_{7/2}$ and $4f_{5/2}$ levels of hafnium in hafnium dioxide. This is further corroborated by the BE difference explained later. Our data, therefore, show that in this type of samples, the presence of suboxide is detected in addition to the dioxide. The suboxide exists till 200 °C. At temperatures around 300 °C, the overlayer is completely oxidized to form HfO_2.

To determine the amount of the dioxide and the suboxide present in the samples, the spectra in the 4f region were fitted with four curves corresponding to the $4f_{7/2}$ and $4f_{5/2}$ levels in the dioxide and in the suboxide. During the curve fitting, the ratio of the areas of the peaks was kept fixed at the statistical ratio 1.4, the FWHM for the dioxide at 2.1 eV, and that for the suboxide of $4f_{7/2}$ level at 1.3 eV. The separation between the $4f_{7/2}$ and $4f_{5/2}$ peaks was locked at the value of 1.7 eV. A combination of Gaussian-Lorentzian was used with about 80% Gaussian. These parameters have been taken from our earlier study [15] and from [12, 13]. An example of curve fitting is shown in Figure 3 for the sample with substrate temperature 100 °C. The areas under the $4f_{7/2}$ peak for both the dioxide and the suboxide were determined from such a curve fitting. The areas were normalized against the total area and are plotted in Figure 4. The suboxide peak clearly shows an initial increase as compared to the as-deposited sample. It is found to remain nearly constant for the 100 and 200 °C samples and is found to disappear for the 300 °C sample. The dioxide peak shows an initial decrease as compared to the as-deposited sample and remains approximately constant for the 100 and 200 °C samples. The data, therefore, show the presence of hafnium suboxide in this type of sample till the substrate temperature of 200 °C. For temperatures around 300 °C, the suboxide disappears and the hafnium overlayer undergoes complete oxidation to form HfO_2.

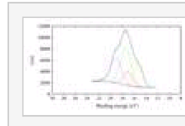

Figure 3: Curve fitting of Hf 4f region in type A sample with substrate temperature of 100 °C. The peaks correspond to $4f_{7/2}$ and $4f_{5/2}$ levels in the dioxide and in the suboxide. The dashed curve shows the fit.

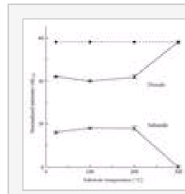

Figure 4: Normalized intensity (in percentage) of the $4f_{7/2}$ peak in the dioxide and the suboxide for type A samples as a function of the substrate temperature. The areas were determined from curve fitting. The error bars are shown. The dashed curve is the total area under the $4f_{7/2}$ peaks.

Figure 5 shows the multiplex spectra in the Hf 4f region for type B samples as a function of temperature. The corresponding oxygen spectra in these samples are shown in Figure 6. Again, these spectra are normalized to have equal intensity at 12.0 eV in the Hf 4f region and at 527.0 eV in the oxygen region. The major peaks in these figures have been aligned. As seen in Figure 5, the shoulder on the right-hand side of the Hf 4f main peak is seen to increase for the 200 °C sample as compared to the 100 °C sample. Some slight variation is observed in the intensity of this region as a function of the substrate temperature. The shoulder is seen to disappear completely for the sample at temperature 600 °C. To determine the temperature at which the suboxide disappears, we have taken data for the sample with substrate temperature of 550 °C. It is observed that the suboxide persists even at 550 °C. The data, therefore, indicate that the suboxide in the annealed samples disappears at temperatures greater than 550 °C. The normalized areas under the $4f_{7/2}$ peak for the oxide and the suboxide have been determined from curve fitting the 4f region. The parameters used are the same as those used for type A samples. These normalized areas are plotted in Figure 7. This figure shows an initial increase in the suboxide as the temperature is increased to 200 °C. No significant variation in the content of the suboxide is observed between the temperature range from 200 to 400 °C. The concentration of the suboxide is seen to decrease at higher temperatures going to zero at 600 °C. The dioxide shows an initial decrease and is found to remain somewhat constant in the temperature range from 200 to 400 °C. At temperatures greater than 400 °C, the dioxide increases. The dashed lines in Figures 4 and 7 represent the total hafnium content as determined from the normalized Hf $4f_{7/2}$ data in both the dioxide and the suboxide. A comparison of the areas in these figures demonstrates that the total amount of hafnium deposited in both types of the samples remains the same. A redistribution of hafnium is observed between the dioxide and the suboxide. The content of the suboxide is

seen to be more in type B samples than in type A samples. However, the dioxide content is observed to be more in type A samples than in type B samples.

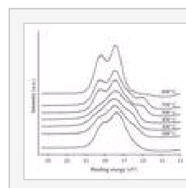

Figure 5: Normalized Hf 4f spectra in type B samples as a function of substrate temperature. The major peaks have been aligned.

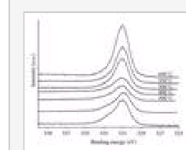

Figure 6: Normalized oxygen 1s spectra in type B samples as a function of substrate temperature. The major peaks have been aligned.

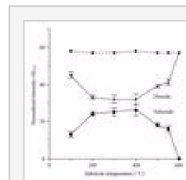

Figure 7: Normalized intensity (in percentage) of the $4f_{7/2}$ peak in the dioxide and the suboxide for type B samples as a function of the substrate temperature. The areas were determined from curve fitting. The error bars are shown. The dashed curve is the total area under the $4f_{7/2}$ peaks.

Xing et al. [11] deposited about 1000 Å film of elemental hafnium on silicon substrates at a base pressure of high 10^{-7} torr using the focused electron beam evaporation technique. The Hf/Si interface was subjected to rapid thermal oxidation process at temperatures ranging from 300 to 700 °C. They have characterized the interface using X-ray diffraction, Auger electron spectroscopy, XPS, and electrical properties. Their results indicate that at oxidation temperatures lower than 500 °C, the film is partially oxidized. The hafnium film is found to be completely transformed to HfO_2 at temperatures above 500 °C. They have also observed an interfacial layer of hafnium silicate between the HfO_2 and silicon substrate. No further investigation on the presence of the suboxide has been performed. In contrast to their study, our data show no chemical interaction between hafnium and silicon up to the temperature (600 °C) investigated in this study. This may be due to the difference in the annealing conditions performed on the samples.

Morant et al. [13] have used XPS to investigate the oxidation of Hf foil by exposing it to oxygen keeping the foil at room temperature. Prior to exposure, they had cleaned the sample surface by ion etching and high-temperature annealing. Despite the cleaning process adopted by them and with a base pressure of $< 10^{-10}$ torr in the chamber, their analysis still showed the presence of some oxygen on the foil. This indicates that hafnium has a strong affinity for oxygen; consistent with our observation that hafnium gets deposited as hafnium oxide(s) at higher pressures. Upon oxygen exposures $\leqslant 5$ L, they observed the formation of hafnium suboxide. Hafnium dioxide was found to be formed at oxygen exposures $\geqslant 10$ L. In their study, no mention has been made about the charge correction to the BEs in the presence of the oxides. Their study shows that the thickness of the suboxide increases to 4 monolayers as the oxygen exposure is increased to ~25 L. This thickness then decreases to a saturation value of ~4Å upon further exposure to oxygen. Their study also shows that the suboxide is present in the sample even at higher exposures of oxygen. Our data demonstrates the presence of the suboxide as a function of the substrate temperature and the complete oxidation of the overlayer at higher temperatures.

Suzer et al. [12] have utilized soft X-ray photoemission spectroscopy to determine the BE shifts and the valence band offsets of HfO_2 grown on Hf metal. In their study, the polycrystalline hafnium foil was kept at a temperature of 200 °C and was exposed to oxygen for various durations. They have observed the formation of hafnium suboxide in addition to the dioxide. The BE difference between the $4f_{7/2}$ peaks in the dioxide and the suboxide has been determined to be 1.7 eV. In our investigation, this difference is seen to be in the range 1.6– 2.8 eV and is found to depend upon the amount of the suboxide present in the sample.

In order to get more information on the formation of the oxides, we have determined the BE difference between the main peak in the oxygen 1s region and the $4f_{7/2}$ peak in the hafnium dioxide as well as in the suboxide. These differences are plotted in Figure 8. The dashed horizontal line in this figure corresponds to the corresponding BE difference value of 513.2 eV in the pure HfO_2 sample, as determined in the previous study [15]. In case of HfO_2, the difference is observed to start from a slightly higher value and shows a decreasing trend as the temperature is increased in type A samples. The expected difference is seen to be reached at temperature above 200 °C. Type B samples show a different behavior. For these samples, the BE difference starts from a higher value and is observed to increase until about 400 °C. For temperatures greater than 400 °C, it decreases sharply reaching the expected value at about 600 °C. The data indicate that the presence of the suboxide produces different surface charging effects in the samples. The charging effect is more pronounced in type B samples (which contain more suboxide) than in type A samples. The presence of oxygen may be attributed to the chemisorbed oxygen on the hafnium wire and/or residual water vapor in the chamber.

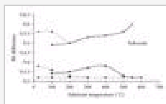

Figure 8: The difference in the BE between the oxygen 1s peak and the Hf $4f_{7/2}$ peak as a function of substrate temperature. The dashed curves correspond to type A samples and the solid curves to type B samples. The dashed-dotted horizontal line at 513.2 eV is the BE difference in the pure HfO_2 sample.

In conclusion, we have compared the formation of the hafnium dioxide and the hafnium suboxide in two types of samples. Elemental hafnium gets deposited as a mixture of the dioxide and the suboxide. The content of the suboxide in type A samples is observed to be more than that in type B samples. The dioxide is found to be more in type B samples than in type A samples. The hafnium overlayer is observed to be completely oxidized to HfO_2 at a substrate temperature of 300°C for type A sample and at 600°C for type B sample. The spectral data also show no chemical interaction between the hafnium overlayer and the underlying silicon substrate under the depositing conditions used in this investigation.

Acknowledgments

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References

1. F. Lime, K. Oshima, M. Cassé, et al., " Carrier mobility in advanced CMOS devices with metal gate and HfO2 gate dielectric," *Solid-State Electronics*, vol. 47, no. 10, pp. 1617– 1621, 2003.
2. A. Deshpande, R. Inman, G. Jursich, and C. Takoudis, " Characterization of hafnium oxide grown on silicon by atomic layer deposition: interface structure," *Microelectronic Engineering*, vol. 83, no. 3, pp. 547– 552, 2006.
3. G. D. Wilk, R. M. Wallace, and J. M. Anthony, " High-κ gate dielectrics: current status and materials properties considerations," *Journal of Applied Physics*, vol. 89, no. 10, pp. 5243– 5275, 2001.
4. S.-W. Nam, J.-H. Yoo, S. Nam, et al., " Influence of annealing condition on the properties of sputtered hafnium oxide," *Journal of Non-Crystalline Solids*, vol. 303, no. 1, pp. 139– 143, 2002.
5. C. J. Först, C. R. Ashman, K. Schwarz, and P. E. Blöchl, " The interface between silicon and a high-k oxide," *Nature*, vol. 427, no. 6969, pp. 53– 56, 2004.
6. V. Sammelselg, R. Rammula, J. Aarik, A. Kikas, K. Kooser, and T. Käämbre, " XPS and AFM investigation of hafnium dioxide thin films prepared by atomic layer deposition on silicon," *Journal of Electron Spectroscopy and Related Phenomena*, vol. 156– 158, pp. 150– 154, 2007.
7. S. Lee and D.-L. Kwong, " Dual poly-Si gate metal oxide semiconductor field effect transistors fabricated with high-quality chemical vapor deposition HfO2 gate dielectrics," *Japanese Journal of Applied Physics*, vol. 42, no. 12, pp. 7256– 7258, 2003.
8. S. Nam, S.-W. Nam, J.-H. Yoo, and D.-H. Ko, " Interface control by modified sputtering on Pt/HfO2/Si system," *Materials Science and Engineering B*, vol. 102, no. 1– 3, pp. 123– 127, 2003.
9. T. P. Smirnova, L. V. Yakovkina, V. N. Kitchai, et al., " Chemical vapor deposition and characterization of hafnium oxide films," *Journal of Physics and Chemistry of Solids*, vol. 69, no. 2-3, pp. 685– 687, 2008.
10. D. Weier, C. Flüchter, A. de Siervo, et al., " Photoelectron spectroscopy (XPS) and photoelectron diffraction (XPD) studies on the system hafnium silicide and hafnium oxide on Si(1 0 0)," *Materials Science in Semiconductor Processing*, vol. 9, no. 6, pp. 1055– 1060, 2006.
11. S. Xing, N. Zhang, Z. Song, Q. Shen, and C. Lin, " Preparation of hafnium oxide thin film by electron beam evaporation of hafnium incorporating a post thermal process," *Microelectronic Engineering*, vol. 66, no. 1– 4, pp. 451– 456, 2003.
12. S. Suzer, S. Sayan, M. M. B. Holl, E. Garfunkel, Z. Hussain, and N. M. Hamdan, " Soft X-ray photoemission studies of Hf oxidation," *Journal of Vacuum Science and Technology A*, vol. 21, no. 1, pp. 106– 109, 2003.
13. C. Morant, L. Galán, and J. M. Sanz, " An XPS study of the initial stages of oxidation of hafnium," *Surface and Interface Analysis*, vol. 16, no. 1– 12, pp. 304– 308, 1990.
14. N. Ohtsu, B. Tsuchiya, M. Oku, T. Shikama, and K. Wagatsuma, " X-ray photoelectron spectroscopic study on initial oxidation of hafnium hydride fractured in an ultra-high vacuum," *Applied Surface Science*, vol. 253, no. 16, pp. 6844– 6847, 2007.
15. A. R. Chourasia and R. L. Miller, " Auger parameter of hafnium in elemental hafnium and in hafnium oxide," *Surface Science*, vol. 573, no. 2, pp. 320– 326, 2004.

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