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Interaction of Hf with Si surface: A wiggler radiation study

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Abstract : Hf deposited on Si(100) resulted in the formation of HfO_2 and some unstable HfO_x by reacting with the residual oxygen. Hf 4f core level exhibited a strong Hf^{4+} and weak Hf^0 signals corresponding to HfO_2 and Hf silicide. Hf dioxide begins to disintegrate when annealed at 800^0C into oxidized silicide. Hf deposited on Si extracts the residual oxygen present in the form of SiO_x O_2 and leads to the formation of $HfO_{2.}$ Reactivity of Hf with oxygen is much higher compared to that of Si with oxygen. Very stable $HfSi_2$ formation occurs after annealing at 800^0C

Keywords : Photoelectron Soectroscopy, Synchrotron radiation, Oxide, Thin film, Annealing

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1. Introduction

Scaling down the capacitor structures in electronic devices used mainly for charge storage requires a smaller and smaller gate oxide thickness. The decrease in thickness of SiO_2 which is a commonly used dielectric material to below 1 nm causes adverse increase in leakage current. Therefore continued scaling demands the use of 1 nm equivalent gate oxide thickness. One possible way to circumvent this problem is to replace SiO_2 with a high-k material. Many alternative dielectric oxides such as Ta_2O_5, HfO_2, Al_2O_3, TiO_2, La_2O_3 etc. have been proposed and examined in the recent past. Most of the high-k materials are unstable on Si when subjected to annealing around 1000^0C and react with Si to form some interfacial oxides or silicides [1] which are usually low dielectric materials. Therefore, the alternative high-k material should be thermodynamically stable on Si apart from having high dielectric constant. Among the high k oxides suggested HfO_2 has been considered as one of the most promising candidates due to its high dielectric constant(k ~ 25), large band gap and high thermal stability [2,3]. HfO_2 thin films were also used as anti reflection coating for Si wave guide components [4].

In the recent past several investigations have been made studying the thermal stability, chemical states, band offsets, electrical and physical properties of HfO_2 layers on Si Substrate [5,6,7]. Decomposition of interfacial SiO_2 was observed during HfO_2 deposition onto oxygen covered Si substrate [8,9,10]. In this paper we report the interaction of very thin (sub nm level) HfO_2 layer deposited onto clean Si(100) surface by XPS technique with intense wiggler radiation. We observed HfO_2 and silicide formation upon depositing Hf at room temperature onto clean Si(100). Upon thermal annealing in oxygen ambient silicide decomposed and a complete transformation into HfO_2 observed. When flashed at 800^0C, Hf dioxide completely decomposed and the silicide re-observed at exactly the same binding energy as in the freshly deposited sample.

2. Experiment

Pure Hf was deposited onto p-type Si(100) substrate using e-beam evaporation technique in-situ in the preparation chamber of THE-XPS machine at BW2 beamline of HASYLAB. Base pressure of the chamber was maintained at 8.0×10^{-10} mbar. These films were oxidized in O_2 ambient of 1.4×10^{-4} mbar at around 300^0C to produce HfO_2. Prior to the deposition Si substrate was flashed at 960^0C until a good p(2×1) LEED pattern was observed. Surface cleanliness of the substrate Si was checked by XPS at grazing X-ray incidence and found no traces of carbon or oxygen. Hf coverage was measured by a crystal balance and found to be in sub nm level. XPS measurements were done at grazing incidence using 3000 eV photon energy with a line width of about 0.5 eV. Bulk Si $2p_{3/2}$ peak position at a binding energy of 99.55 eV was used for energy calibration.

3. Results and Discussion

Hf dioxide film thickness was estimated using the emission angle dependent yield of Si 1s and Hf $3d_{3/2}$ core levels and the data is shown in Figure 1. Open circle represents the experimentally observed ratios and the solid curve shows the calculated ratios using layer attenuation model [11] for a layer of thickness 7.7Å. Calculated data is in excellent agreement with the experimentally observed data indicating a sharp interface without intermixing of Si and HfO_2.

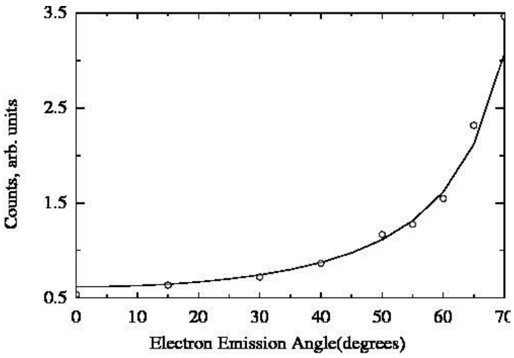

Fig. 1: The emission angle dependence of Si 1s to Hf $3d_{5/2}$ intensity ratio

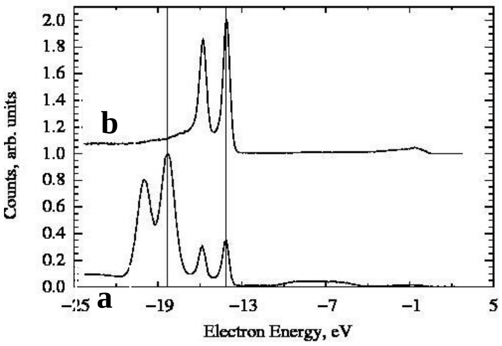

Fig. 2: Hf 4f and valence band of (a) as deposited and (b) annealed at 800^0C HfO_2/Si(100)

Figure 2 shows the VB with Hf 4f spectra of Hf deposited onto Si(100). As deposited Hf thin film exhibits a complex structure between 20 and 14 eV binding energy. Hf being highly reactive to oxygen readily produced Hf oxide with residual oxygen coming from the evaporator. Oxidation at 300^0C exhibited a 4f doublet with no low B.E. shoulder indicating complete oxidation of deposited Hf. $4f_{7/2}$ peak position of this doublet is at a B.E. of 18.01 eV. Due to higher reactivity of Hf to oxygen compared to that of Si, Hf deposition removes oxygen bonded to Si and forms stable HfO_2. This is the reason for strong oxide peaks observed on as deposited sample compared to silicide peaks observed at low binding energy. After flashing the sample at 800^0C, HfO_2 disappeared and only silicide peaks are observed. These observations indicate that $HfSi_2$ is thermally stable upto 800^0C.

References

[1] K. J. Hubbard and D. G. Schlom, J. Mater. Res. **11**, 2757 (1996).

[2] G. D. Wilk, R. M. Wallace and J. M. Anthony; J. App. Phys. **89**, 5243(2001).

[3] Seung-Gu Lim et.al; J. Appl. Phys. **91**, 4500 (2002).

[4] M. Alvisi, S. Scaglione, S. martelli, A. Rizzo, L. Vasallelli; Thin Solid Films, **354**, 19 (1999).

[5] R. P. Pezzi, J. Morais, S. R. Dahmen, K. P. Bastos, L. Miotti, G. V. Soares, I. J. R. Baumvol, F. L. Freire, Jr.; J. Vac. Sci. Technol. A **21**, 1424 (2004).

[6] Yongjin Wang, Zhilang Lin, Xinli Cheng, Haibo Xiao, Feng Zhang, Shichang Zou; Appl. Surf. Sci. **228**, 93 (2004).

[7] M. Oshima, S. Toyoda, T. Okumura, J. Okabayashi, H. Kumigashira, K.Ono, M. Niwa, K. Usuda and N. Hirashita, Appl. Phys. Lett. **83**, 2172 (2003)

[8] M. Copel and M. C. Reuter; Appl. Phys. Lett.; **83**, 3398 (2003).

[9] S. J. Wang, P. C. Lim, A. C. H. Huan, C. L. Liu, J. W. Chai, S. Y. Chow, J. S. Pan, Q. Li and C. K. Ong; Appl. Phys. Lett. **82**, 2047 (2003).

[10] S. Zaima, N. Wakai, T. Yamauchi and Y. Yasuda; J. Appl. Phys. **74**, 6703 (1993).

[11] L. I. Johansson, C. Virojanadara, Th. Eickhoff, W. Drube; Surface Science, **529**, 198 (2003).