Thermally induced structural changes in nanoporous silicon dioxide from x-ray photoelectron spectroscopy

Martin T. K. Soh*1
Woodside Energy Ltd., Perth 6000, Australia

J. H. Thomas III
Characterization Facility, University of Minnesota, Minneapolis, Minnesota 55455

Joseph J. Talghader
Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota 55455

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Morphological changes due to adsorbed gases in nanoporous silicon dioxide thin films are demonstrated using in situ x-ray photoelectron spectroscopy at temperatures in the range 20≤T≤300 °C. Adsorbed hydrogen bonded water vapor is observed to relax the surface bond strain of low-temperature electron-beam deposited silicon dioxide up to 100 °C. This was determined by measuring the width of the Si 2p and O 1s photoemission peak full widths at half maximum, which are distinctly smaller for films with adsorbed water vapor than for the same films after vapor has been outgassed by heating above 100 °C. In situ heating in the range 100<T<200 °C decreases the peak width as the atoms gain sufficient energy to establish a more homogeneous local bonding environment. This process is overshadowed above 200 °C as thermally induced localized bond strains and charge inhomogeneities at the surface begin to introduce disorder, as demonstrated in the repeatable increase in peak spread with temperature for thermally grown silicon dioxide and quartz. The in vacuo peak width behavior in subsequent thermal cycles is repeatable for the nanoporous thin films. However, if the films are reexposed to atmosphere, the initial increase in peak width is seen again. © 2006 American Vacuum Society. [DOI: 10.1116/1.2359734]

I. INTRODUCTION

Silicon dioxide (SiO2), in particular, its low-temperature deposited nanoporous polymorphs (np-SiO2), has been studied extensively for device passivation and optical coatings.1 The low-packing density and moisture permeability of such films are well known,2 which has led to alternative deposition schemes to avoid these issues.3,4 While such characteristics are usually undesirable, they imply that one might be able to trap adsorbed gases using encapsulation, thus controlling stress and perhaps other mechanical properties. This capability would be particularly useful in the design of coatings on membranes in micromechanical devices, which makes comprehension of the precise mechanisms behind such characteristics critical to device design and fabrication.

In the present work, in situ x-ray photoelectron spectroscopy (XPS) has been used to study the full width at half maximum (FWHM) dependence of Si 2p and O 1s peaks as a function of temperature of electron-beam deposited np-SiO2, thermally grown SiO2, and α quartz. It has been found that the FWHM of np-SiO2 during the first thermal cycle in vacuo is due to the desorption of hydrogen bonded water vapor resulting in subsequent bond angle strain relaxation at the surface. This is contrasted with the thermal and quartz samples that do not follow this behavior, that is, the FWHM increases with temperature indicating an increase in bond angle strain. After the initial desorption process of water from np-SiO2 occurs, the FWHM indicates a reproducible decrease in bond angle strain and relaxation. These data have been shown to be reproducible run to run and for different depositions. Re-exposure to ambient strongly suggests that any thermally induced bond reconfiguration in np-SiO2 is not permanent.

II. EXPERIMENT

np-SiO2 thin films of 200 nm thickness were deposited from fused silica granules onto 0.5 mm thick (100) silicon substrates, as well as 0.13 mm thick (100) germanium substrates, in a Varian 3118 electron-beam evaporator at room temperature. Chamber base pressure was 3×10−7 Torr, and the deposition rate was set at 1 nm s−1 using an Inficon quartz-crystal monitor. A 200 nm thick dry thermal oxide was also grown at 1100 °C on a (100) silicon substrate using a Tylan furnace for comparison. XPS was performed on a Physical Electronics 555 system using a cylindrical mirror analyzer. Survey (1000≥E≥0 eV, 100 ms/step, 0.5 eV/step, and 200 eV pass energy) and high-resolution spectra (10 eV window, 100 ms/step, 0.05 eV/step, and 25 eV pass energy) were obtained as a function of probe temperature. The system binding energy scale was calibrated using a gold (Au) and copper (Cu) standard to yield Au 4f7/2, Cu 2p3/2, and carbon C 1s photoelectron binding energies of 83.85, 932.68, and 285 eV, respectively. The FWHM of the Au 4f7/2 peak was 1.18 eV. XPS specimens were mechanically mounted onto a low-temperature heating stage, with the

*Electronic mail: martin.soh@woodside.com.au.
stage temperature measured from an attached $K$-type thermocouple. The heater ramp rate was approximately 1 °C/min up to 300±1 °C, and the chamber pressure was <1.5 $\times$ 10$^{-7}$ Torr.

XPS survey spectra of all specimen surfaces yielded Si, O, and C photoemission peaks, with the integrated area of the C 1s peak monotonically decreasing with increasing measurement temperature. An 85% Gaussian curve fit was applied to high-resolution scans of the Si 2p and O 1s peaks after the background was subtracted using the Shirley algorithm (Fig. 1 for the np-SiO$_2$ thin films). From Fig. 1, there was no evidence of peak structure. The model curve fitted well to the experimental data, justifying the single peak parameter fitting approach taken.

III. RESULTS AND DISCUSSION

Figure 2 plots the FWHMs of the Si 2p and O 1s photoemission peaks of the np-SiO$_2$ thin films, thermally grown oxide, and quartz substrate versus temperature. These data suggest a monotonic reduction in Si 2p and O 1s FWHMs to a value of 1.87 and 1.89 eV (at ~200 °C), respectively, for the np-SiO$_2$ thin films after the first heating cycle. This is in contrast to the increase in FWHMs of the thermal oxide and quartz specimens. The O 1s and Si 2p peak binding energy difference was measured over the entire temperature range to be 429.38±0.01 eV for the np-SiO$_2$ thin films, 429.37±0.02 eV for the thermally grown oxide, and 429.43±0.02 eV for the quartz. This indicates that the O 1s and Si 2p binding energy chemical shifts are not significantly affected by heating ($20\leq T\leq300$ °C).

np-SiO$_2$ specimens deposited onto Ge substrates also display the behavior of Fig. 1, and FWHM measurements taken at the beginning and end of a 2 h anneal cycle at all measurement temperatures >60 °C were found to be the same. Furthermore, the negligible impact of carbon resulting from ambient exposure on the FWHM was confirmed by constant O 1s/Si 2p and C 1s/Si 2p integrated area ratios (Fig. 4). FWHM measurements during temperature cycles were repeatable for all specimens, with the exception of first cycle behavior for the np-SiO$_2$ thin films—observable again post-anneal after prolonged exposure to the ambient.
The evidence suggests that the FWHM versus temperature observations are a result of surface bonding reconfiguration. According to Grunthaner et al., thermally grown SiO$_2$ consists of a continuous network of Si-centered tetrahedra joined together by oxygen atoms with an average Si–O–Si bond angle, corresponding to a certain O $1s$ and Si $2p$ binding energy displacement and ring size. A decrease in ring size will reduce the average Si–O–Si bond angle and increase the O $1s$ and Si $2p$ chemical shifts, while an increase in ring size will produce the opposite effect. Since the O $1s$ and Si $2p$ binding energy difference was observed to be invariant to temperature and heat treatment in Fig. 3, the average Si–O–Si bond angle is independent of annealing temperature. However, the increase in FWHM with temperature for the thermal oxide specimen indicates that the distribution of bond angles and ring sizes at the surface broadens with temperature. This suggests that thermally induced localized bond strain and charge inhomogeneities on the thermal oxide and quartz surfaces are prevalent at elevated temperatures, making the surface more chemically reactive and vulnerable to etching (formation of silanol groups and failure, for example, in humidity). It is clear that *ex situ* measurement of Si $2p$ and O $1s$ FWHMs after annealing will not reveal this behavior.

In contrast, the np-SiO$_2$ Si $2p$ and O $1s$ FWHMs versus heat treatment in Fig. 2 exhibit a different first cycle behavior. The np-SiO$_2$ FWHM versus temperature behavior in subsequent temperature cycles is repeatable and rises to a significantly higher value at 20 °C, which may be a result of (water) impurity desorption. The average bond angle of the np-SiO$_2$ thin films is analogous to those of the thermal oxide and quartz substrates due to similar O $1s$ and Si $2p$ chemical shifts. However, the variation in bond angle (and ring size) distributions is much more pronounced in the np-SiO$_2$ thin films because of the larger peak FWHM at 20 °C. This may be due to lower packing density in thin films deposited at reduced temperatures, with low adatom mobility at the surface resulting in highly disordered bonding (large FWHM). Therefore, it is likely that hydration of the np-SiO$_2$ thin film surface serves to stabilize the morphology through interatomic bond strain relaxation—already observed for np-SiO$_2$ thin films deposited by electron beam at room temperature and 200 °C. The as-deposited bond strains are rein-

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**Fig. 3.** O $1s$–Si $2p$ binding energy chemical shifts vs temperature for the (a) np-SiO$_2$ thin films, (b) thermal oxide, and (c) quartz substrate. The error bars denote the standard deviation.

**Fig. 4.** O $1s$/Si $2p$ vs C $1s$/Si $2p$ area for the (a) np-SiO$_2$ thin films, (b) thermal oxide, and (c) quartz.
stated upon dehydration, increasing the FWHM in the first heating cycle up to 100 °C. Above 100 °C, the FWHM will begin to decrease as the atoms gain sufficient energy to establish a more homogeneous ring configuration. However, this process is overshadowed at higher temperatures due to the mechanisms already established for the thermal oxide and quartz. The FWHM monotonically increases upon cooldown (due to the absence of water desorption) that explains previous observations of higher Si 2p and O 1s peak FWHMs from immediate ex situ XPS post-anneal.15

The ex situ adsorption and thermal desorption of water into and out of np-SiO2 thin films have been postulated by many workers through infrared absorption studies.1,3,16 The permanent reduction in Si–OH (stretching) infrared absorption intensity around 3350–650 cm−1, as well as peak shift and FWHM reduction of the Si–O (stretching) absorption mode around 1070 cm−1 from annealing,17 has been attributed to the removal of physisorbed silanol groups (through Novak condensation18) and thermally induced morphological changes. However, the XPS peak FWHM first cycle and temperature characteristic of the np-SiO2 thin films (Fig. 2) were reproducible after re-exposure to the ambient, suggesting that any thermally induced bonding reconfiguration (for T \( \leq \) 300 °C) is not permanent. Given that the first cycle behavior only extends to T=100 °C, the XPS analysis indicates that the mechanism of bond strain relaxation hydration in np-SiO2 is through much weaker hydrogen bonding.

IV. CONCLUSIONS

In situ XPS was used to study the Si 2p and O 1s FWHM temperature dependence of np-SiO2 thin films, thermal oxide, and quartz. It was found that np-SiO2 bond distributions go through a reversible change with temperature where it is proposed that water vapor is desorbed in vacuo for T < 100 °C. After this process occurs, the material continues to show a relaxation in bond angle distribution (through reduced peak FWHM). This was compared with both the thermal oxide on silicon and quartz, which exhibit an increase in bond angle distributions to T=300 °C. Thermal cycling in vacuo of these materials is reproducible. With ambient exposure, the np-SiO2 film is reexposed to moisture and the initial cycle is reproduced as well as the higher temperature dependence (due to bond angle relaxation).

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