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Ultra-thin oxide growth on silicon during 10 keV x-ray irradiation

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ABSTRACT

Surface effects on silicon wafers irradiated by 10 keV x-rays at room temperature were characterized using x-ray photoelectron spectroscopy and spectroscopic ellipsometry. The samples were exposed to total ionizing doses ranging from 1.0 to 12 Mrad(SiO_2) at x-ray dose rates ranging from 5.8 krad(SiO_2)/min to 67 krad(SiO_2)/min. Accelerated thin oxide growth on irradiated samples compared to natural native oxide growth under room temperature conditions was demonstrated, and the composition of the irradiation-accelerated oxide was investigated. The presence of suboxides along with silicon dioxide was confirmed on the irradiated silicon sample. Two thin oxide growth models were applied to characterize the enhanced oxidation rate observed for irradiated wafers.

1. Introduction

Advances in nuclear technology have led to increased utilization of radiation sources for energy generation, material characterization, and health diagnostics. Unintended exposure to radiation can have harmful consequences to both personnel and electronic equipment. Radiation effects on the electronic properties of common semiconductors such as silicon, including charge trapping, carrier lifetime degradation, and variation in breakdown voltage have been extensively studied [1,2]. Fewer studies have focused on the materials property changes in silicon upon radiation [3,4]. In recent work, we demonstrated that 10 keV x-rays are capable of inducing accelerated oxide growth on silicon [5]. However, a comprehensive investigation of the surface effects of x-ray irradiated silicon, including an analysis of the thin oxide composition and growth rate, has not been performed.

Accurate characterization of thin oxide films is challenging. Measurement techniques such as spectroscopic ellipsometry (SE), x-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM) are often used to determine the thickness of silicon dioxide; however, in the case of very thin oxides, all of these techniques are challenged by the presence of an intermediate suboxide layer. Precise knowledge of the composition and dielectric properties of this layer is required to determine the overall thickness accurately. TEM is the most direct technique for measuring the physical thickness of the thin oxide layer, but TEM measurements are sensitive to sample preparation, are expensive and time-consuming, and analyze only a very small area on the sample. XPS, on the other hand, is relatively accurate in determining the thickness of oxides < 3 nm, but it also measures only a small area (~0.125 mm^2) of the sample and is a relatively time-consuming measurement. SE, on the other hand, can be performed over a large sample surface area (~8 mm^2) and has been used extensively for oxide measurements on films of thickness greater than ~10 nm due to its fast and repeatable performance that is non-destructive to the sample. However, in the case of very thin oxide films, SE measurements tend to overestimate the thickness [6,7].

In this report, we comprehensively study the thickness, and composition of the ultra-thin oxide layer that is grown during room temperature x-ray radiation exposure of a silicon wafer through a combination of XPS and SE. A systematic offset is shown for oxide thickness estimates by XPS and SE, from which we conclude that SE can be used to conveniently and non-destructively track the evolution of irradiation-induced oxide growth. Following the experimental studies, two thin oxide models are applied to investigate possible mechanisms behind the observed enhancement in oxidation rate due to irradiation: (1) the Elovich model, which has previously been applied to native oxide growth on silicon at room temperature [8], and (2) an oxide growth model developed by Massoud et al. [9], which extends the Deal–Grove linear-parabolic model to encompass thin oxides formed on silicon at elevated temperatures.

2. Experimental setup and methodology

P-type silicon (boron; resistivity 0.01–0.02 Ω-cm) samples with a <100> crystal orientation were used in this study. Prior to irradiation, the samples were cleaned in a 20% dilute hydrofluoric acid (HF) solution

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for 1 min, followed by an ethanol rinse. Each irradiation run consisted of two samples; one sample was exposed to 10 keV x-rays and the other was used as a control to determine the influence of the ambient environment in the absence of irradiation.

The silicon samples were irradiated using a 10 keV x-ray source (ARACOR Model 4100) with a 3-centimeter diameter beam. The sample to be irradiated was placed in the beam on a stage 4 cm away from the source. The irradiation was performed in air. Dose rates ranging from 5.8 krad(SiO_2)/min to 67 krad(SiO_2)/min were used, with a total exposure time of 180 min at each dose rate. During the irradiation, the sample temperature was raised by 3–4 °C observed using a thermistor, which is not significant enough to impact oxidation. Consequently, all irradiation experiments are considered to be performed under standard temperature and pressure conditions. Across the different irradiation runs, the ambient temperature and humidity were found to vary on a day-to-day basis from 68 to 77 °F and from 42% to 71%, respectively. The oxidation growth observed on the irradiated samples was consistently greater than the corresponding non-irradiated reference samples, indicating that the variation in ambient conditions had little influence on the oxide growth rate compared to the radiation.

XPS measurements were performed to study the influence of irradiation on the surface chemistry and the Si/SiO_2 transition layer. A 180° spherical capacitor energy analyzer-based instrument (Physical Electronics VersaProbe 5000) was used for all XPS analyses presented in our work. Analyses were acquired using a monochromatic 100 μm diameter 25 W Al Kα x-ray beam rastered over a 250 μm by 500 μm area. The analyzer was operated in the constant pass energy mode. A take-off angle of 65° off sample-normal was used. Survey and high-resolution spectra were recorded at pass energies of 187.8 eV and 23.5 eV, respectively. The spectrometer was calibrated to the Au4f7/2, Ag3d5/2, and Cu2p3/2 peaks at 84.05, 368.28, and 932.65 eV, respectively. No additional oxide growth was possible during the XPS measurements, which are performed under vacuum conditions.

Oxide thickness was estimated ex-situ using spectroscopic ellipsometry (SE) (J. A. Woolam M-2000) and XPS. For SE, the initial oxide thickness of each sample was measured within 30 min of the HF cleaning step. Ellipsometrically estimated initial oxide thicknesses ranged from 6 to 13 Å, likely due to sample-to-sample variation and differences in ambient conditions during sample preparation. The bulk silicon dioxide refractive index model was employed in all SE measurements for consistency and simplicity. As discussed in Section 3.1.2, SE estimates of oxide thickness were found to differ from XPS thickness estimates by a nearly constant offset. Hence, even though they do not directly provide a highly accurate measurement of ultra-thin oxide thickness, the SE measurements provide a useful and practical method to track and parameterize changes in oxide thickness for the x-ray irradiated samples.

3. Results and discussion

3.1. Surface characterization of irradiated silicon

3.1.1. XPS compositional analysis of irradiation-induced oxide

Fig. 1 shows XPS Si 2p spectra acquired from the irradiated silicon samples. Two main peaks are shown: the peak near 99.8 eV corresponds to the binding energy of silicon and the peak near 103.4 eV corresponds to the oxide film on the silicon surface. The increasing size of the peak centered near 103.4 eV for samples exposed to increasing x-ray dose rates indicates that silicon samples exposed to higher dose rates of x-ray irradiation for a fixed duration of time have thicker oxide films grown on the surface. The control sample that was not irradiated only shows a clearly defined silicon peak. The oxide peak of a sample irradiated at 31.5 krad(SiO_2)/min for 3 h was analyzed to determine the presence of stoichiometric and non-stoichiometric oxide compounds. As shown in Fig. 1(b), SiO_2 is the dominant constituent of the oxide film, but suboxides, e.g., Si_2O_3, SiO, and Si_2O, are also likely present at the film/substrate interface. The suboxide composition showed no correlation with x-ray dose rate. Suboxide transition layers are known to be present between a silicon substrate and bulk silicon dioxide film for traditional oxide growth conditions as well as native oxides, and pose a particular challenge for accurately measuring the thickness of thin oxides [10–13].

3.1.2. Thin oxide thickness estimation and comparison between XPS and ellipsometry

XPS and SE measurements were conducted to quantify the thickness of x-ray irradiation-induced oxide grown on the silicon samples. Thickness values obtained from the two different measurement tools were compared to determine whether the less accurate but more convenient, non-destructive SE measurements would be suitable for use in the oxide growth models discussed in the next section.

Oxide thickness values determined using SE are based on the change in polarization of reflected s- and p-polarized light from a sample. The measurement is performed across a range of wavelengths and is expressed in terms of two parameters: an amplitude ratio, Ψ, and the phase difference, Δ. The governing relation for the parameterization of the measurement is shown in Eq. (1), which relates the Fresnel reflection coefficients for p- and s-polarized light, r_p and r_s, to Ψ and Δ, respectively. The experimentally measured values of r_p and r_s are compared to theoretical estimates based on a user defined model of the film stack. The estimates of r_p and r_s, are a function of the refractive index and

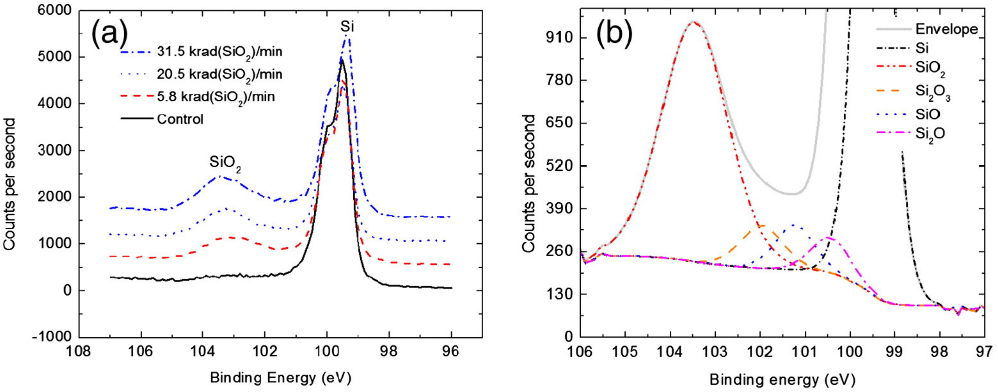

Fig. 1. (a) Si 2p spectra acquired from silicon samples irradiated at dose rates of 5.8 krad(SiO_2)/min, 20.5 krad(SiO_2)/min and 31.5 krad(SiO_2)/min for 180 min each. A spectrum acquired from a control sample placed in the same ambient conditions without irradiation is included as a reference. The spectra corresponding to different dose rates are offset for clarity. (b) Si 2p spectrum acquired from a sample irradiated at 31.5 krad(SiO_2)/min for 3 h suggests the presence of suboxides in addition to stoichiometric SiO_2.