Electron Spin Resonance Study of a New Positively Charged Defect in Device Oxides Damaged by Soft X-Rays

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The use of vacuum soft X-ray (VXR) exposure to efficiently generate paramagnetic defects in thin oxide layers is described. Positive charge reactions are observed. Hydrogen is found to react with $E'$ to form a related defect called the 74-G doublet which is positively charged like the $E'$. The doublet can be easily destroyed by exposure to ultraviolet light in contrast to the $E'$ which is comparatively stable. This new positive defect is a likely intermediate in positive charge annealing. The chemical reactions associated with the defect explain some of the differences observed between oxides damaged by high fields and by radiation. The defect fits into the most completely proposed mechanism for interface state formation.

1. INTRODUCTION

Electron spin resonance (ESR) experiments have previously identified two paramagnetic defects designated the $E'$ and $P_b$ which have subsequently been correlated with positive charge in the oxide and interface states respectively at the SiO$_2$/Si interface. 1,2,3 A third defect, hyperfine split by the presence of a nearby proton and commonly called the 74-G doublet, has recently been observed in large quantities in SiO$_2$/Si samples damaged with soft X-rays. 4,5 In this talk we concentrate on the chemical reactions involving the $E'$ and the doublet as observed with ESR and capacitance-voltage (C-V) measurements. The $P_b$ will not be discussed in this talk.

2. EXPERIMENT

The silicon substrates were 100 mm diameter n-type (111) wafers with resistivities of about 180 ohm-cm. Oxide was grown in dry oxygen with 3% HCl at 1000 C to a thickness of about 1630 A. The wafer for all of the samples studied in this talk was not hydrogen annealed and was labeled n-(111)-05 in reference 4. The technique of vacuum X-ray (VXR) exposure was used to damage the samples. An Anelva research electron beam evaporator was used as an X-ray generator by focusing a 3.9 keV electron beam on a W target in a vacuum better than $1.5 \times 10^{-6}$ torr. Figure 1 shows the X-ray power absorbed in both a thick SiO$_2$ target and a thin SiO$_2$ layer of 1400 A when 100 mamp of electron beam current is used. Our samples were damaged with 70 mamp and a total beam energy of 1870 kJ was put into the W target (1.92 hour exposure time). This procedure is expected to produce a total exposure of about $2 \times 10^{10}$ rad with a mean energy of about 0.6 to 0.8 keV in the thin SiO$_2$/Si samples and about $30 \times 10^{10}$ with a mean X-ray energy of about 1.7-2.0 keV for a thick target. The important point about VXR exposure at low accelerating voltages is the shallow X-ray penetration in the samples so that damage is relatively concentrated in the thin oxide and activation of unwanted paramagnetic contaminants in the thick silicon substrate is minimized.
Fig. 1. Calculation of power absorbed in thick and thin SiO$_2$ exposed to a W X-ray flux in vacuum.

Fig. 2. ESR spectra taken on X-ray damaged SiO$_2$/Si with the (111) axis oriented perpendicular to the magnetic field. The labels A1, A1+UV1, and A1+UV1+A2 refer to spectra taken on the sample after sequential forming gas anneal at 100 C, ultraviolet light exposure, and second forming gas anneal at 100 C.

3. RESULTS

Figure 2 (reproduced from reference 5) shows how the ESR spectrum for a damaged sample is modified by alternating forming gas (A1, A2, ...) and ultraviolet light (UV1, UV2, ...) exposures. The forming gas (5% H$_2$/95% N$_2$) anneals were performed at 100 C for 3 minutes. Ultraviolet light was provided by the full spectrum output of a 250 watt Hg arc lamp at a distance of 4 cm for 1 minute in air. Figure 3(b) shows a more complete plot of the E' and 74-G spin densities obtained by double numerical integration of the ESR resonances as a function of these treatments. Figure 2(a) was obtained from a damaged sample which had only been rinsed in deionized water (DI) for 3 minutes to remove surface paramagnetic contamination. The E' spins in the oxide were then partially converted to 74-G doublet by the 3 minute exposure to forming gas at 100 C. As shown in Fig. 3(b), 61% of the E' spins convert to doublet and 39% remain as E'. However, as shown in Fig. 3(a), the sum of E' and 74-G doublet remains unchanged (within the accuracy of the data). The 74-G doublet can also be
efficiently and selectively annihilated with a 1 minute exposure to ultraviolet light with little disturbance to the E'. This effect is shown in the ESR spectra in Fig. 2(b) and (c) and also plotted in Fig. 3(b). Although the UV exposure destroyed 80% of the 74-G doublet, the remaining 20% were reconverted to E' as shown by inspection of the data plotted for E' at points A1 and UV1 in Fig. 3(b). About 48% of the E' remaining at this point can be converted to doublet with a second 3 minute forming gas anneal and substantially annihilated with a second UV exposure.

A plot of net positive charge in a sample damaged during the same X-ray exposure is shown in Fig. 3(a). This sample was identically treated in all respects except that it was back coated with aluminum after damage and rinsing and used for high frequency (1 MHz) C-V measurements. The flatband voltage data used to obtain the net positive charge points in Fig. 3(a) were determined from an average of several C-V curves taken with a Hg probe across the length of the sample and using the experimental observation (from an etchback experiment on a third identically damaged and treated sample) that the E' and 74-G doublet are distributed approximately uniformly throughout the oxide thickness.4,5 Comparison of the charge of net positive charge curve in Fig. 3(a) with the ESR data for the E', 74-G doublet, and the sum of the E' and doublet in Fig. 3 shows that agreement is possible if and only if the positive charge is the sum of the E' and doublet. Thus the 74-G doublet is positively charged like the E'. Moreover, since both E' and doublet are positively charged, observation of the formation of the doublet and thus characterization of SiO2/Si can apparently not be achieved with electrical measurements alone.

Since the VXR technique produces damage extending only about 1 micrometer deep, the E' and 74-G reactions can be studied in "bulk" materials as if they were damaged films approx-

imately 1 micrometer thick. Preliminary experiments in the SiO2 material "wet" Suprasil (1200 wt. ppm OH) were performed. Figure 4 compares ESR spectra for our thin SiO2/Si sample after forming gas anneal with an identically treated bulk Suprasil sample. Although the behavior is quite similar in the two cases, only 33% of the E' converted to doublet in the Suprasil case compared with 61% in the case of SiO2/Si. The 74-G doublet was also annihilated by a 1 minute UV exposure without disturbance to the E' in an identical behavior to that observed in SiO2/Si. This interesting result implies that the usual explanation of photoelectron injection from the silicon does not appear to be the UV driven mechanism for the annihilation of the paramagnetic activity of this defect on uncoated oxide in air (it could still be the basis of the charge neutralization since paramagnetism can be destroyed independently of charge).

Fig. 4. (a) ESR spectrum of X-ray damaged thin SiO2 after forming gas anneal. (b) ESR spectrum of identically treated Suprasil rod.

4. DISCUSSION

Warren and Lenahan6 recently detected the E' in samples damaged with a positive electric
The experiments above suggest the 74-G doublet is a key intermediate in hydrogen assisted positive charge annealing of SiO₂ and must also be a good candidate for such a role in all processes correlated with the presence of hydrogen, namely, interface state formation and interface state annealing. Griscom, using an extensive set of published literature, has recently concluded that the buildup of interface states in SiO₂/Si is correlated with the diffusion of radiolytic molecular hydrogen and proposed a model based on this conclusion. In one reaction path of this model, E' somehow reacts with molecular hydrogen to release monatomic hydrogen (Eq. 8 of ref. 7) which then reacts with Si-H bonds at the interface to form interface states. But Eq. 8 is not quite correct or complete because the reaction of molecular hydrogen and E' forms 74-G doublet. However, making the single substitution of the doublet for monatomic hydrogen or a presursor of monatomic hydrogen in Griscom's argument, results in the same interface state formation mechanism but now with a very easily identified state immediately preceeding interface state formation.

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REFERENCES