Electron Spin Resonance Analysis of EP Center Interactions With H_2: Evidence for a Localized EP Center Structure

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Abstract

We report the first observation of a hydrogen complexed EP (E'δ) center. Analysis of EP/H and E'γ/H electron spin resonance spectra show that they have quite similar doublet splitting, doublet linewidth, and doublet g-shift from the center line, providing the first evidence that EP (E'δ) centers do not have a delocalized structure.

I. INTRODUCTION

Hole traps dominate the electronic properties of amorphous SiO_2 thin films. Recent studies have suggested that hole traps [1] and H_2 [2] participate in the formation of interface traps at the Si/SiO_2 boundary. These studies are consistent with the McLean proton drift model [3]. It has been shown that there is a rough one to one correspondence between hole traps and E'γ centers (an oxygen vacancy related defect consisting of an unpaired electron localized on a silicon backbonded to three oxygens) in the gate oxides of gamma irradiated MOS devices [4-6] and that E'γ centers play an important role in hole trapping in separation by implanted oxygen (SIMOX) buried oxides [7]. It was recently demonstrated that exposure to H_2 at room temperature results in the rapid transformation of E'γ centers into two H complexed defects [8]. Since a buildup of interface traps occurred on the same time scale as the E'γ / H_2 reactions, it was concluded that E'γ center hole traps play an indirect role in interface trap formation [9,10].

Recently, a new type of E' center, which we provisionally term EP (E for E', and P for Provisional assignment), has been reported in a wide variety of thin SiO_2 films [11-15]. A recent study [11-13] has extensively characterized the electronic behavior of EP (or E'δ) defects in thermal oxides: they are electrically active with large capture cross sections for electrons and holes and can participate in hole trapping. Although EP centers do not contribute significantly to radiation induced positive charge due to their instability, spatial distribution, and large electron capture cross section, they may play other roles in MOS oxides. For example, EP centers are responsible for approximately 20% of SIMOX E' centers [14], may play a role in interface trap formation, and may participate in enhanced low dose rate gain degradation in bipolar devices [16]. Since EP defects may play important roles in MOS oxides, it is of interest to determine their physical structure.

The center's electron spin resonance (ESR) spectra resembles the E'δ spectra reported in bulk SiO_2 by Griscom and Friebele [17]. Griscom and Friebele's proposed E'δ center model consists of an unpaired electron delocalized over a cavity of Cl capped Si. While recent thin film experiments suggest that Cl is not involved [11-14], no strong evidence exists for the structure of the EP (E'δ) center in thin films. A thin film EP (E'δ) model has been proposed in which the unpaired electron is delocalized over a silicon microcluster [14]. This model has neither been confirmed nor proven wrong; EP structure remains unknown. The most direct way to establish the structure of an SiO_2 defect is through ESR detection of the defect's ^{29}Si hyperfine spectra. However, detection of the ^{29}Si hyperfine spectra is notoriously difficult in thin films. A less direct method would be to study hydrogen hyperfine interaction.

We demonstrate for the first time the conversion of EP centers in the presence of H_2 at room temperature into hydrogen complexed EP/H centers. It was not previously known whether EP centers would react with H_2. We find that the EP/H_2 reaction occurs rapidly at room temperature, suggesting a possible role for EP centers in interface trap formation in some oxides. We compare EP/H_2 with E'γ/H_2 reactions and find close similarities between the EP/H doublet spectra and the previously studied E'γ/H 74G doublet ESR spectra [8-10,18,19]. Our results demonstrate a localized spin for the EP/H defect. The similarities between the EP/H doublet spectra and the E'γ/H 74G doublet ESR spectra suggest that the structure of the EP center is similar to the structure of the E'γ center and thus, contrary to a recent proposal [14], not "delocalized".

II. EXPERIMENTAL DETAILS

Our study utilized SIMOX buried oxides since it is possible to preferentially generate quite high densities of either EP or E'γ centers in these films [7]. The single implant n(100) 385nm SIMOX samples received a total oxygen dose of $1.8x10^{18}/cm^3$ at an energy of 200 keV, a current of 34 mA, and an implant temperature of 640°C. After implantation, the buried oxide was annealed at 1315°C for 5 hours in 99.5% argon and 0.5% oxygen. Before any measurements were taken, a residual oxide and the silicon overlayer were removed by subsequent room temperature etches in HF and KOH. ESR measurements were performed at room temperature on an X-band spectrometer. H_2 exposures were performed at room temperature in forming gas (10% H_2, 90% N_2).

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III. EXPERIMENTAL RESULTS

Narrow field unscaled ESR traces in Fig. 1 show that (a) extended exposure to vacuum ultraviolet (VUV) illumination ($hc/\lambda \leq 10.2$ eV) generates a very strong ($\sim 5 \times 10^{12}/cm^2$) E'_γ signal while (b) very brief exposure to filtered VUV ($hc/\lambda = 10.2$ eV) with positive potential across the oxide generates a very strong ($\sim 1 \times 10^{12}/cm^2$) EP signal [9,15]. Substantial fractions of both of these E'_γ and EP centers are positively charged when paramagnetic [7,11-13].

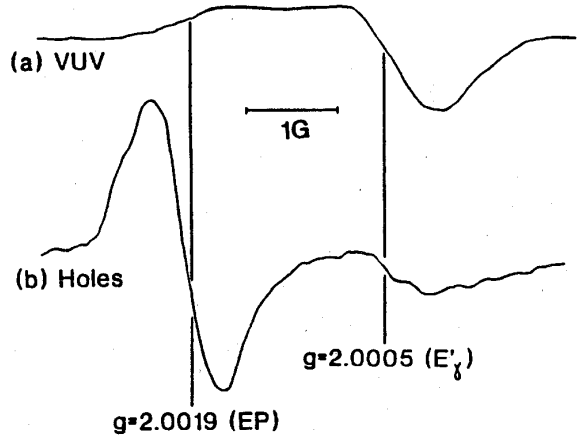

Fig. 1: ESR traces of SIMOX oxides after (a) 50 hours of VUV illumination without bias and (b) injection of approximately 5×10^{13} holes / cm^2.

In Fig. 2, ESR traces encompassing a wider field than Fig. 1 illustrate the effects that a subsequent 2 hour room temperature H_2 exposure has on the samples from Fig. 1. The H_2 exposure was performed at room temperature in forming gas (10% H_2, 90% N_2). The strong center lines in Fig. 2 correspond to (a) E'_γ and (b) EP signals. The close side peaks in (a) are due to the so called 10.4 G E'_γ/H complex [18]. In both cases weak doublets are generated, separated by 74G about the E'_γ in (a) and separated by 78 G about the EP center in (b). These doublet spectra were not detected before H_2 exposure. The doublet spectra indicate the interaction of the E' unpaired electron with hydrogen. The doublet arises because the 100% abundant I=1/2 hydrogen magnetic nuclei split the local magnetic field into two components, resulting in the two line spectra. We also observe a decrease in the intensity of the EP and E'_γ center lines. The decrease in center line intensity is comparable to the increase in doublet density. This numerical correspondence indicates that in both cases, the H_2 exposure results in the conversion of E' centers into hydrogen complexed E' centers. We find that both conversion reactions take place in minutes and saturate within two hours at room temperature, suggesting a role for both E' variants in the interface trap formation process. The similar time scale also suggests a similar structure for E'_γ and EP centers. (Since hydrogen doublets are split in two by the hydrogen hyperfine interaction and since spin densities ($\sim 1\text{-}5 \times 10^{11}/cm^2$) are an order of magnitude lower that for standard E' signals, the hydrogen complexed defects are difficult to observe. ESR traces are thus shown after saturation (~2 hours) of the E'/H_2 reactions.)

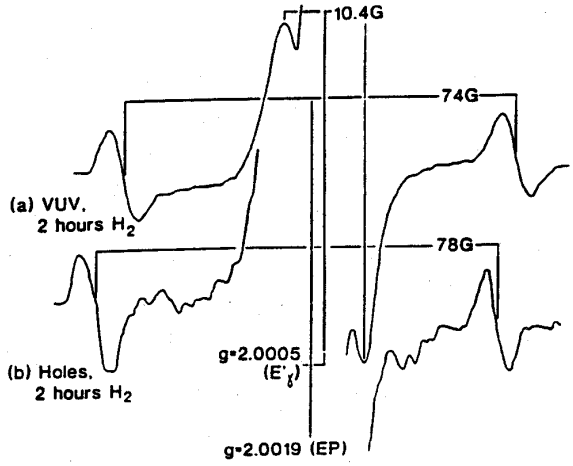

Fig. 2: Wide field ESR traces of the oxides from Fig. 1 after a subsequent two hour exposure to H_2.

The E'_γ/H 74G doublet (an E'_γ center in which one of the backbonded oxygens is replaced by a hydrogen) has an effective g = 2.0014, very close to the value reported by Vitko [19]. This effective g shift from the center line at g=2.0005 is somewhat greater than that predicted from the Breit-Rabi correction (which one would expect if the E' electron wavefunction were otherwise unperturbed by the hydrogen). Vitko [19] and Tsai and Griscom [18] have noted that the 74G separation suggests about 15% localization on the hydrogen, consistent with very strong localization on a central silicon.

The EP/H 78G doublet has an effective g=2.0036, a shift from the center line at g=2.0019 again somewhat greater than one would expect from the Breit-Rabi correction but roughly comparable to that observed for the E'_γ/H doublet. The 78G splitting, consistent with the earlier suggestions of Vitko [19] and Tsai and Griscom [18] regarding the 74G doublet, suggests a nearly identical localization on the hydrogen. As in the case of the E'_γ/H 74G doublet, this suggests very strong localization of the unpaired electron on one atom.

IV. DISCUSSION

Comparing the two hydrogen complexed E' spectra reveals similar doublet splitting, as well as similar doublet g-shift from center, and doublet linewidth. These close similarities between the EP/H complex spectrum and the E'_γ/H complex spectrum combined with the similarity of the hydrogen reaction rates indicates similar defect structures. The close correspondence in doublet splitting suggests that, as in the E'_γ case, the EP unpaired electron is quite strongly localized on a single atom. Strong localization on a single central atom does

not support the current delocalized silicon microcluster model of the EP (E'δ) centers in thin films. An absolutely conclusive identification of the EP center awaits observation of the ^{29}Si doublet spectra.

Earlier studies have shown that a decrease in E'γ density as a result of room temperature E'γ/H reactions takes place on the same time scale (minutes) as a comparable increase in interface trap density [9,10]. Since EP/H reactions also occur on this same time scale, they too may be involved in the post stress interface trap formation process. Further experiments, including a close comparison with electrical measurements, will be needed to establish this relationship.

Although we still do not have enough experimental evidence to propose a specific structural model for the EP center, it is interesting to speculate as to what the structure of the EP center might be. It is likely, as we have shown, to be similar to the E'γ center. Like the E'γ, the EP center saturates at low microwave power, has a g-tensor with components that deviate only slightly from the free electron, and interacts with H_2 on the same time-scale as does E'γ at room temperature. In addition, the doublet splitting of the H complexed EP center indicates strong localization on a single atom as in the case of the E'γ. The fact that the g-tensor components of the EP center (all are $\approx$2.0019) deviates from the free electron g (2.0023) less than that of the E'γ center ($g_{//} \cong 2.0018$, $g_{\perp} \cong 2.0000$) may provide a structural clue. The very small deviation from the free electron g indicates very low spin orbit coupling of the unpaired electron with the central atom. Low spin orbit coupling suggests a small central atom, possibly an atom smaller than Si. An unpaired spin associated with an oxygen deficient silicon with a slightly different environment than the E'γ center is, of course, a very likely candidate. We also can also rule out many other possibilities and identify another possible suspect. Aluminum, Na, F, B, N, Be, Li, and H can all be ruled out because these nuclei all have 100% abundant magnetic moments which would split the spectra into two or more lines. Oxygen can be ruled out because unpaired spins on oxygens generally exhibit broad ESR spectra whereas the EP is quite narrow. Ne and He are noble gases and can be ruled out. Since we do not believe there is a significant concentration of Mg present, we tentatively rule out Mg. Carbon however cannot be ruled out and, in fact, would be a suitable alternative to silicon since it has the same chemical strucure as silicon.

V. CONCLUSIONS

We have presented the first substantial evidence that EP (E'δ) do not have a highly delocalized unpaired electron. Our results suggest that EP centers are not silicon microclusters but are more closely related to conventional E'γ centers, indicating that EP is an appropriate designation. The fact that EP/H_2 reactions take place at room temperature and on a time scale similar to E'γ/H reactions suggests that EP centers may also play a role in interface trap formation in some oxides.

VI. ACKNOWLEDGMENTS

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