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Production of E'_δ center induced by dry heat treatment of nonburied SiO_2 films

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Electron paramagnetic resonance data demonstrate that E'_δ, a radiation-induced defect consistently found in buried oxide films, can also be generated in nonburied oxides after heat treatment in a sufficiently dry ambient. The center appears in samples heated in either N_2 or O_2 with moisture content on the order of 1 part per million. The near equality of the number of E'_δ centers in the N_2 and O_2 treated samples implies that the presence of O_2 does not reduce the number of precursor defects. The results suggest that the center is related to a deficiency of hydrogen-related species in the ambient rather than an O_2 deficiency as has been previously suggested. © *1996 American Institute of Physics.* [S0003-6951(96)00227-6]

Decades of studies on thermally grown microelectronic grade SiO_2 films indicate that high temperature heat treatment in an inert ambient can produce beneficial as well as deleterious results. An anneal at temperatures greater than 900 °C generally enhances the performance of a gate oxide, but it deteriorates oxides sandwiched between two layers of silicon (a buried oxide).[1,2] Although electrical measurements constitute the most direct method of addressing oxide reliability, electron paramagnetic resonance (EPR) spectroscopy has been effective for studying many types of oxides including buried oxides formed by oxygen implantation into silicon (SIMOX) or compression bonding of thermally oxidized silicon wafers (BESOI).[3] Two major defects are revealed in the buried oxides: the E'_γ center, an oxygen vacancy related defect commonly observed in irradiated bulk and thin film amorphous SiO_2, and the E'_δ center, most likely a multiple oxygen vacancy defect. Although no one-to-one correspondence between buried oxide defects and the failure of devices built on buried oxides has been demonstrated, studying the chemistry of these centers may lead to the cause of the deteriorated electrical response of BESOI and SIMOX as well as polysilicon gated structures.

The focus of this work is E'_δ, a center initially identified in bulk silica by Griscom[4] and later in thin films by a group studying the buried oxide in SIMOX wafers.[5] Although a definitive description of E'_δ does not yet exist, it is generally accepted that the center consists of a delocalized electron shared by four Si atoms at a vacancy in SiO_2.[4,5] Other than SIMOX, the oxide layer of BESOI wafers, thermal oxides coated with polysilicon, and a variety of thermal oxides without the Si overlayer have exhibited this center.[5–7] Most of the data suggest that E'_δ is generated during the high temperature treatment of an oxide film buried underneath a layer of Si, but observation of the center in the nonburied oxides questions this conclusion. To determine the conditions that lead to the formation of the E'_δ center, we systematically examine a variety of oxide films heated to 1000 °C in different ambient. The results indicate that the E'_δ concentration in nonburied oxides is greatly increased after heat treatment in dry N_2 or O_2. The latter is particularly significant because it indicates that the generation of E'_δ is strongly associated with the absence of a hydrogenous species rather than oxygen as has been recently proposed.[8,9]

The majority of the samples used for this study consists of 400 nm thick steam oxides grown at 850 °C on a (100) silicon substrate. In addition, some samples received a polysilicon overlayer by exposing the oxide to 300 mTorr SiH_4 at 650 °C. Samples were heated in air, Ar, N_2, or O_2 at 1000 °C for 5 h. The treatments were conducted in an open tube furnace (standard treatment), or a sealed double-walled furnace for which the moisture level was on the order of 1 part per million (ppm) at 1000 °C (dry treatment). After the dry treatment, the samples were cooled to room temperature in the dry ambient. All samples were irradiated with x rays to a dose of 1 Mrad. Selected samples were subsequently annealed at 200 °C.

All EPR spectra reported here were taken one day after 1 Mrad x-ray irradiation. We identify the E'_δ center in terms of its g value, which is obtained from the experimental spectrum through the expression, $g = \nu h/\mu_b B_{\mathrm{zero}}$. Here ν is the microwave frequency, h is Planck's constant, μ_b is the Bohr magneton, and B_{zero} is the zero crossing of the first derivative of the absorption. Further study of E'_δ in our samples shows that it exhibits isotropic symmetry, saturates at about 0.02 mW, and is diminished by a factor of 5 after a 200 °C air anneal as is expected for the E'_δ center.[4,5] In the nonburied oxides, the absolute density of E'_δ obtained by comparison to a standard is about 2×10^{11} cm^{-2}, or about 25% that observed in the buried version of the same oxide.

Figure 1 summarizes the results of this investigation regarding the radiation-induced signals, the E'_γ center with $g = 2.0005$ ($B_{\mathrm{zero}} = 3497$ G) and the E'_δ center with $g = 2.0019$ ($B_{\mathrm{zero}} = 3495$ G). Figure 1(a) depicts an EPR spectrum of a buried oxide treated in N_2 in the open furnace. Except that the amplitude is smaller by a factor of 4, the spectrum is similar to that taken on SIMOX and BESOI buried oxides subjected to identical treatments. Figure 1(b) represents the nonburied oxide subjected to identical heat treatment and irradiation. The density of the E'_γ center is less than 10^{11} cm^{-2} as is expected for a film irradiated to a dose of only 1 Mrad. Argon and air treatments produce similar null results. Figures 1(c) and 1(d) reveal the presence of the E'_δ center in the nonburied oxide films heated in dry ambient

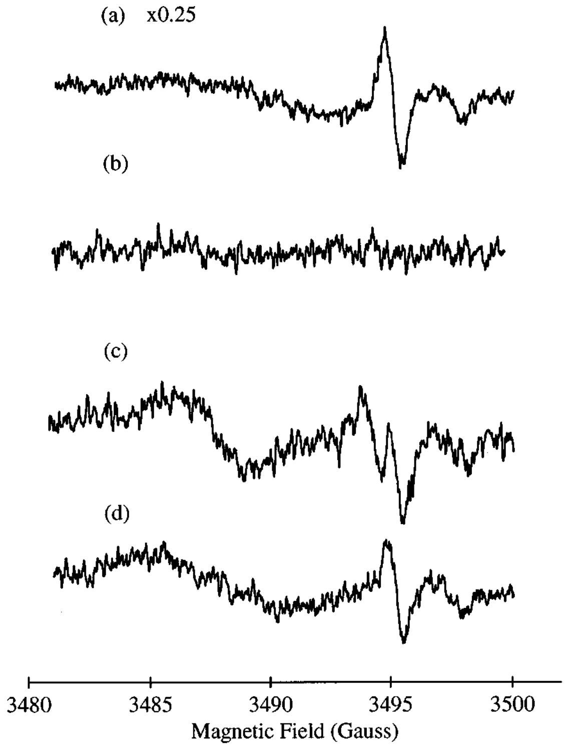

FIG. 1. EPR spectra taken after 1 Mrad x-ray irradiation on (a) buried oxide with standard treatment, nonburied oxides with (b) standard treatment, (c) dry N_2 treatment, and (d) dry O_2 treatment. All heat treatments were at 1000 °C for 5 h. Data in (a) have been multiplied by 0.25.

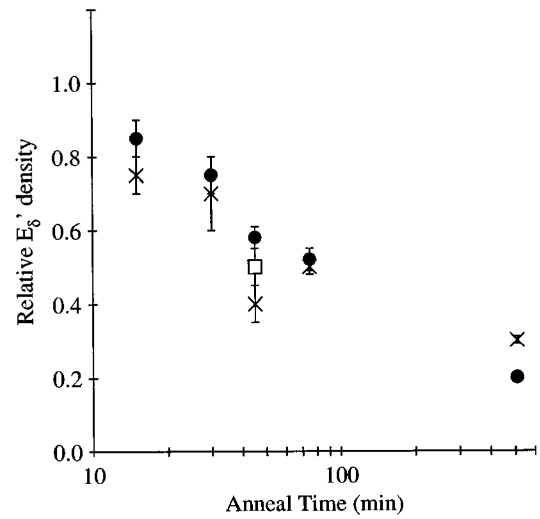

FIG. 2. Time dependence for annealing E'_δ at 200 °C in air: ●, SiO_2 film on Si; ×, Si/Si O_2/Si sandwich; □, SiO_2 film annealed in dry ambient. Density is relative to that of an unannealed sample.

and demonstrate the conditions necessary for generation. Different from the film in Fig. 1(b), the film represented in Fig. 1(c) was heat treated in N_2 with less than 1 ppm ambient moisture and that in Fig. 1(d) was heated in O_2 with about 1 ppm moisture content. Comparison of Figs. 1(b) and 1(c) shows that the E' centers are sensitive to the amount of ambient moisture present during a high temperature treatment. Figures 1(c) and 1(d) indicate that the number of centers does not vary as the ambient gas is changed from dry N_2 to dry O_2. Thus, elimination of moisture appears to be essential for the generation of the E' centers. Furthermore, we conclude that removal of hydrogen, not oxygen, from the moist ambient is essential for defect formation.

Several other features concerning Fig. 1 should be noted. First, although measurable in both buried and nonburied oxides, the number of E' centers is lower in the nonburied oxides by a factor of at least 4. Second, we observe that the dry treatment with H_2O levels as high as 5 ppm produced the E' centers; however, opening the dry furnace at 600 °C resulted in no measurable centers. Lastly, several additional centers appear in the dry N_2 treated films. In Fig. 1(c), for example, two features are apparent to the left of the E'_δ center. The centers, which are more clearly resolved using different EPR signal parameters, have been only casually studied at this time and appear to be associated with the Si substrate rather than the oxide. Further discussion will be deferred to a future publication.

Figure 2 illustrates the role of moisture during annealing of the E'_δ center. The density in nonburied oxides (filled circles) and buried oxides (crosses) was measured as a function of anneal time at 200 °C in room ambient. In addition, the E'_δ density in two nonburied oxides was measured after a 45 min dry N_2 anneal. The average of the two measurements is represented by the unfilled square in Fig. 2. If ambient moisture were a factor in E'_δ annealing, we would expect the anneal rate for the buried and nonburied oxides to differ because the overlying polysilicon should inhibit H_2O diffusion to the oxide. Thus, the buried and nonburied data sets with the support of the single data point from the dry anneal suggest that ambient moisture does not affect the annealing kinetics of E'_δ. It should be noted that, unlike the situation following hole injection,[10] there was no indication of an increase in the E'_γ signal as the E'_δ signal diminished. Rather, the E'_γ density remained constant throughout the anneal.

The point defect concentration in buried oxide films is thought to be related to the presence of the top silicon layer.[5,8,9] In particular, Devine and coworkers have suggested that generation of the E'_δ and E'_γ centers is related to the limited oxygen supply at the buried oxide/Si interface during the high temperature treatment and to the subsequent outdiffusion of oxygen from the oxide.[8,11] Much data appear to support the outdiffusion model. For example, infrared measurements show that O interstitials in the overlying Si layer increase during high temperature heat treatment of a buried oxide structure.[11] The association between O deficiency and the production of E'_δ is further supported by postirradiation reoxidation studies that show a reduction in the E' centers after reoxidation.[5] Finally, the outdiffusion model is consistent with the proposed multiple oxygen vacancy defect structure.[4,5] However, a study of the temperature required to generate the centers suggests that diffusion could not solely account for the defect generation and introduces the possibility of SiO production via reduction of the buried oxide.[9]

The assumption permeating the defect generation models cited above is that the Si top layer prevents ambient oxygen from reaching the oxide layer. However, Si also prevents ambient moisture from diffusing to the buried oxide. The presence of the E'_δ center in a nonburied oxide treated in dry O_2 [Fig. 1(d)] clearly demonstrates that minimization of O_2 is not linked to E'_δ generation. Rather, H_2O or some other hydrogen-related species must be responsible. This is in agreement with the early work on silica containing chlorine. The samples that exhibited the greatest E'_δ density also contained the least H and OH species.[4] The influence of moisture is also consistent with the studies that show a decrease in E'_δ following reoxidation because, unless extreme measures are taken, moisture would be added during the oxidation and, thus, quench E'_δ production.[5] However, the observation of the centers in dry oxygen treated nonburied oxides does contradict the existing defect generation models. Since the same number of E'_δ centers was observed in N_2 and O_2 treated films, it is unlikely that the center arises from O outdiffusion or the formation of SiO. The former model is based on a concentration gradient of oxygen between the oxide and ambient, which is obviously greatly decreased by the O_2 treatment. The latter model is based solely on the low O_2 partial pressure present at the surface of a buried oxide. This clearly is not the case during the O_2 treatment.

Data taken for this investigation show that the intensity of the E'_δ signal is smaller by a factor of 4 in the nonburied oxides compared to that seen in the buried films. It is unlikely that different room temperature annealing rates for buried and nonburied films can account for this behavior since the data of Fig. 2 reveal similar annealing rates at 200 °C for both oxides. Rather, the different concentrations may result from differing levels of moisture established by the Si coating on the buried oxide and the dry heat treatment of nonburied oxide. Alternatively, since the E'_δ center is thought to be located primarily near the interfaces, the factor of 4 density decrease may be related to the factor of 2 decrease in number of Si/SiO_2 interfaces. The present data are insufficient to resolve this issue.

The primary result of this work is that the generation of the E'_δ center in SiO_2 is related to the dryness of the ambient during a high temperature heat treatment and not to the deficiency of oxygen during the treatment as previously thought. Although this does not affect the proposed model of the defect as a multiply oxygen vacancy center, it does highlight the importance of hydrogenous species in the generation of the E'_δ center. Interestingly, moisture in the ambient does not appear to influence the annealing kinetics. Although no model for defect generation is presented at this time, the work clarifies that the E'_δ center is one of a growing number of defects in which the elimination of a hydrogen species is critical for observation of the center by EPR.

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