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Charge state of paramagnetic E′ centre in thermal SiO_2 layers on silicon

V V Afanas'ev and A Stesmans

Department of Physics, University of Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium

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Abstract. Comparison between the densities of positive charge and paramagnetic E′ centres ($O_3{\equiv}Si^{\bullet}$ defects) generated in thermal SiO_2 layers on Si by 10 eV photons at different electric field strengths in the oxide demonstrates that the paramagnetic states cannot be associated with positively charged centres, i.e., the E′ centre is neutral. The variation in E′ density results from the balance between activation by irradiation and passivation with radiolytic hydrogen. Therefore, the neutral diamagnetic state of the defect is ascribed to the $O_3{\equiv}Si$–H fragment in the SiO_2 network, which is converted into an E′ centre by radiation-induced hydrogen cracking.

Since their first observation by Weeks in 1956 [1], electron spin resonance (ESR) active E′-type centres have become the most intensively studied defects in SiO_2. Identification of their atomic kernel as the $O_3{\equiv}Si^{\bullet}$ fragment, where the dot symbolizes an unpaired electron in an sp^3-hybridized orbital of a silicon atom, led to numerous attempts to associate the electronic and optical properties of crystalline and amorphous silicon dioxide with the presence of E′ centres [2]. In particular, the radiation-induced buildup of positive charge in thin SiO_2 layers thermally grown on Si has been found to correlate with generation of paramagnetic E′ centres [3–5]. Importantly, the effective cross section of hole trapping in SiO_2 ($\sigma = (3\text{–}4) \times 10^{-14}$ cm^2, if the Coulombic interaction is taken into account [6, 7]) appears to be the same as that of E′ centre creation [8], suggesting hole trapping at the E′-centre precursor as the rate-limiting step in the radiation-induced charge buildup. The observation that the density of E′ centres decays during ultraviolet (UV) illumination has been associated with neutralization by electrons injected from the Si substrate, and was considered as definitive proof that the E′ centres are positively charged when paramagnetic [4, 5]. Therefore, the E′ centre in thermal oxide on Si has been associated with the E'_{γ} variant in which the paramagnetic $O_3{\equiv}Si^{\bullet}$ fragment faces the positively charged $^{+}Si{\equiv}O_3$ unit, and the radiation-induced positive charging of SiO_2 has been simply described as hole trapping by oxygen vacancies ($O_3{\equiv}Si$–$Si{\equiv}O_3$ defects) in the oxide [4].

Although widely accepted for more than a decade, this simple picture has been questioned by a number of works on the basis of experimental observations of positive charge without an accompanying E′ signal [9] or with a charge density far exceeding that of E′ [10–12], the existence of E′ centres without positive charge [8, 13–15], or even with a reversed charge–paramagnetism relationship [14, 16]. It has been suggested that not only E'_{γ} centres, but also E'_{β} defects (isolated $O_3{\equiv}Si^{\bullet}$ fragments) which are neutral in the paramagnetic state may be present in the oxide depending on preparation conditions [17]. It needs to be added, though, that a large number of these works deal with deposited [9, 13, 14], buried [10, 11, 16] or heavily irradiated oxides [15, 17]; yet there is also substantial evidence that the hypothesis about the positively charged paramagnetic E′ centre fails in as-grown thermal oxides. For instance, the

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repeatedly reported observation that the density of positive charge trapped on centres with capture cross section of $\sigma = (3\text{–}4) \times 10^{-14}$ cm^2 may far exceed the density of the E′ centres available in thermal oxide [11, 12] straightforwardly excludes the simple hole trapping by an O vacancy picture as the universal origin of positive charge. Next, the neutralization cross sections of two 'positively charged' E′-like centres appear to be different by one order of magnitude (10^{-13} cm^2 and 10^{-14} cm^2) [8]. So, taking into account that the electron capture cross section by an attractive centre is determined only by electron–phonon interaction inside the Coulomb potential well which is insensitive to the particular defect structure [18], the transition of E′ to a diamagnetic state is likely determined by a factor different from electron trapping. For example, interaction of an E′ centre with hydrogen was also shown to turn these centres into the diamagnetic state [19, 20]. The latter factor is of particular importance because in most of the experiments, an electric field across the SiO_2 layer has been applied using a corona discharge in air [4, 8, 13, 14, 17]: it has long been known that the positive corona ions in this case are proton complexes with water molecules $(H_2O)_nH^+$, where n depends on relative humidity and ranges from 2 to 5 [21]. Upon neutralization with UV light these complexes release atomic H which may interact with E′ centres in the oxide. Also, UV illumination may lead to a photolysis of water adsorbed at the oxide surface resulting in an additional H supply. Finally, E′ centres were observed even in 5 nm thick oxides [22] in which any presence of trapped holes is excluded because they are neutralized by electron tunnelling from Si and metal [23, 24].

The discrepancy between the expected behaviour of a positively charged centre and the observed characteristics of the E′ defect, as well the possible interference of hydrogen, prompted us to re-examine the relationship between the trapped hole charge and the paramagnetic E′ centres in thermal oxides on Si. First, it will be demonstrated that the E′ centres show no Coulomb attractive interaction with electrons which means that the centre is *neutral* in the paramagnetic state. Second, we will show that the density of paramagnetic E′ centres is primarily sensitive to the concentration of *atomic H* in the oxide during irradiation. The same behaviour is observed both in as-grown and thermally degraded SiO_2 layers on (100) Si, suggesting that in both cases the dominant type of E′ centres in thermal SiO_2 is similar to the E'_β variant in bulk SiO_2.

Two types of sample (A and B) were prepared on 2×9 mm^2 slices of 70 μm thick p-type (100) Si wafers. After standard surface cleaning they were oxidized in dry O_2 at 970 °C to an SiO_2 thickness of 60 nm. For the A-type samples the oxidation was terminated by cooling down in O_2 and they were expected to contain defects *inherited from the oxidation process*. The samples of type B were instead subjected to a 1 h post-oxidation anneal at 970 °C in a mixture of Ar + 10% H_2 in order to generate *additional* oxide defects in the O-free ambient. After the oxide removal from the backside by wet etching, metal–oxide–semiconductor (MOS) structures were prepared by thermoresistive evaporation of gold in vacuum: a semitransparent 13 nm thick Au layer was evaporated on top of the oxide and a ~0.2 μm thick layer was deposited on the backside to provide an ohmic contact to the Si substrate.

The fabricated MOS structures were irradiated with 10 eV photons obtained from a Kr resonant discharge lamp with MgF_2 window. The use of the low photon energy, which exceeds the oxide bandgap only by ~1 eV, firmly excludes knock-off of Si or O atoms from oxide network sites. During irradiation a bias voltage (V_g) was applied to the semitransparent Au electrode to provide an oxide field in the range of −3 to +3 MV cm^{-1}. The density of injected electron–hole pairs was monitored by integrating the photocurrent at the highest fields. After injection of ~10^{15} pairs cm^{-2} into the oxide, the trapped charge density was determined using the flatband voltage shift (ΔV_{FB}) of 1 MHz capacitance–voltage (C–V) curves measured at room temperature. As can be seen from the kinetics of hole trapping at the oxide field of +1 MV cm^{-1} shown

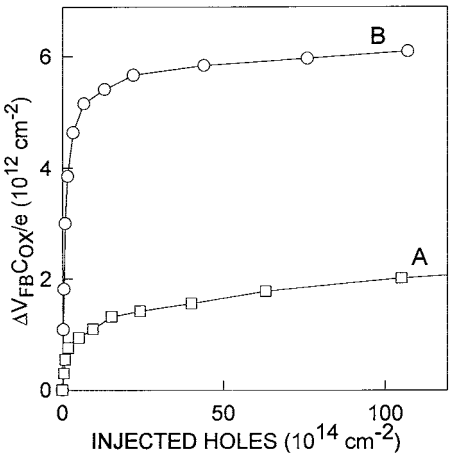

Figure 1. The density of positive charge trapped in the oxide as a function of the injected hole density at +1 MV cm^{-1} oxide field in samples A (□) and B (○). Lines are guides to the eye.

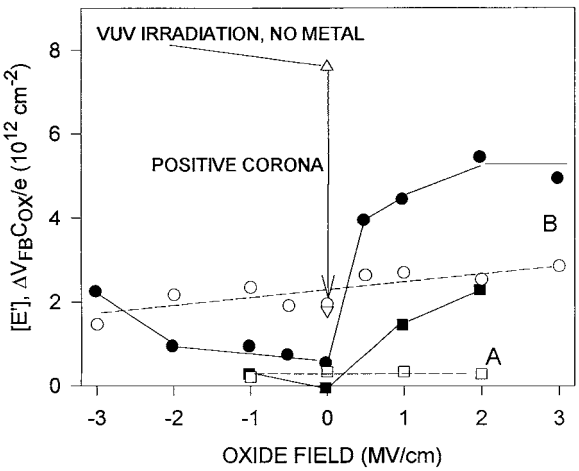

Figure 2. Densities of E′ centres (○, □) and the positive charge (●, ■) observed after injection of 10^{15} electron–hole pairs per cm^2 as a function of the strength of the electric field for MOS structures with as-grown (A: □, ■) and degraded (B: ○, ●) oxide. The effects of VUV irradiation of a non-metallized sample B (△) and subsequent 30 min positive corona exposure (▽) on the E′ centre density are shown for comparison. Lines are guides to the eye.

in figure 1, the charge density saturates after injection of $\sim 10^{15}$ holes cm^{-2} in both sample types. The density of E′ centres also saturates at this injected hole flux without, however, creation of additional E′ centres [15], i.e., the E′ centres analysed here are produced by activation of existing precursor sites. The spatial location of the positive charge was characterized using their neutralization by electrons photoinjected from the Si substrate as described elsewhere [6, 12]. The centroid of the charge distribution was found to be at 5 ± 1 and 7 ± 2 nm from the Si/SiO_2 interface in samples A and B, respectively. This means that most of the hole traps are located near the Si/oxide interface and its density can be calculated from the C–V curve shift with an accuracy of about 10%. The absence of a substantial charge build-up in the bulk of the oxide or near the Au/SiO_2 interface is independently affirmed by the stability of the hole photocurrent through

the oxide during the photoinjection. The preferential hole trapping near the Si/SiO_2 interface agrees with the results of previous studies [6, 11, 12, 25, 26]. Some samples were irradiated without pre-metallization of the oxide and then exposed to the positive corona discharge in air in an experimental arrangement similar to that described by Weinberg [27]. K-band (∼20.1 GHz) ESR observations were made on stacks of ∼20 samples after removal of the metallization in *aqua regia* at 40 °C. The ESR measurements were performed at 4.3 K in the adiabatic slow passage adsorption mode. The absolute spin densities were determined relative to an Si:P marker as described previously with an accuracy of about 15% [15]. After ESR measurements, some of the samples were re-metallized, and C–V measurements were repeated in order to verify the stability of the trapped charge; the charge was found to be unchanged within 10% accuracy. That the metal etching procedure did not have any significant impact on the density of E′ centres was also indicated by ESR measurements on samples irradiated prior to metallization and etching.

The principal results are compiled in figure 2, showing the density of positive charge (filled symbols) and the density of E′ centres observed at $g = 2.000\,55$ (open symbols) in samples type A (squares) and B (circles) as a function of the electric field strength in the SiO_2. The charge density exhibits a considerable field dependence, typical for the radiation-induced charges in Si MOS structures. The reduction of the charge density near zero field is related to efficient neutralization of trapped holes with electrons because the neutralization cross section increases at low field for a Coulomb attractive trap [18, 29]. In contrast, the density of E′ centres in the present samples (both types) shows no drop near zero field, and weakly increases as the field varies from negative to positive. This dependence can be explained by E′ generation by either holes and/or by excitons with close generation cross sections. Obviously, the behaviour of the E′ centres is quite dissimilar to the behaviour of the positive charge, which indicates that there is no Coulomb interaction between E′s and electrons in the oxide.

A second feature revealed by the data in figure 1 is that the density of positive charge observed at positive gate voltage is considerably higher than the saturated density of E′ centres. With decreasing V_g, the charge density strongly decreases while the variation in the E′ density is marginal. In contrast, irradiation without metal on leads to an approximately fourfold increase in the E′ density (open triangle in figure 1) *without any substantial oxide charging*. Taking into account that the density of electron traps in the studied oxides is below 5×10^{11} cm^{-2} as revealed by UV electron photoinjection experiments, charge compensation is firmly excluded. Thus, the density of *neutral* E′ centres is determined by a balance between their irradiation-induced activation and some factor sensitive to the presence of the metal electrode. It has been shown previously that the concentration of radiolytic atomic H in the oxide is affected by the presence of the metal on top of SiO_2: the latter may act as a barrier for H out-diffusion [15] and/or a source of H released by excited electrons [30]. If the sample with the bare oxide is subsequently exposed to positive corona in air for 30 min (without irradiation), the intensity of the E′ signal decreases dramatically, as also indicated by the inverted open triangle in figure 2. Again, this happens without oxide charging which affirms the absence of substantial electron trapping. Therefore, we associate the observed decrease in the E′ density with some action of atomic H produced during corona exposure or irradiation. Worth noticing here is that in the samples irradiated with metal on, about 75% of the E′s remain diamagnetic and neutral, which suggests that they are passivated with H. Apparently then, the E′ centre has a large cross section for H trapping. Probably, H is strongly bonded to the E′ centre: we found that a soak in H_2 of the samples containing neutral E′ centres leads to a ∼50% decrease in the E′ density (without any significant charge variation), which suggests that the formation of $O_3{\equiv}Si$–H through H_2 molecule cracking is energetically favourable.

The above results clearly show that most of the E′ centres in thermally grown oxide on Si are in a neutral state when ESR active, and that they strongly interact with hydrogen. An

obvious model in this case for the E′ centre precursor is the H-terminated centre $O_3{\equiv}Si{-}H$, which may be in an isolated form similar to the E'_β defect in amorphous SiO_2 [2] and to the E'_2 centre in α-quartz [31], or in the form of an H-passivated oxygen vacancy $O_3{\equiv}Si{-}H$ $H{-}Si{\equiv}O_3$ [10, 15]. Probably, the $O_3{\equiv}Si{-}H$ centre constitutes the known hole trap with a capture cross section of 3×10^{-14} cm^2, and releases hydrogen in the form of a proton upon hole trapping. The proton, in its turn, can be trapped in the oxide and give rise to trapped positive charge and donor-like interface states. The neutral E′ centre left behind may be passivated again with radiolytic H or with H_2 thus 're-entering' the hole trapping process. In this way, it may produce multiple trapped holes (protons) as observed experimentally [10]. Accordingly, the total trapped charge will be dependent *on both* the E′ centre density and the concentration of radiolytic hydrogen in the oxide. Indeed, both trends have been reported in the literature (cf [32] and [33], respectively). In fact, the proposed scenario of charge trapping unifies the proton hypothesis of McLean [34] and the model of Dressendorfer and Lenahan in which E′ centres account for hole trapping [3]. According to the advanced picture, the E′ centre represents the most efficient site of proton generation during hole injection or irradiation and, therefore, determines the charge buildup rate which, however, depends also on radiolytic hydrogen concentration.

Potentially, the E′ centre may also trap a hole and may be converted to a diamagnetic positively charged $^+Si{\equiv}O_3$ centre. This defect has been suggested to account for the positive charging of the high-temperature grown [14] and deposited oxides on Si [13], as well as for H_2 cracking [35]. The variation in density of these centres with applied electric field would follow the behaviour of the positive charge in figure 1, i.e., the density of paramagnetic E′ defects would anti-correlate with the charge density (see, e.g., [14]). As a dependence of this kind is not observed here within the accuracy of the experiment, we conclude that the positive charged diamagnetic state is not present in any significant density. Apparently, the probability of interaction of the E′ centre with hydrogen is larger than the probability of hole trapping in our case. However, if the H concentration is reduced, as it may be in the structures with a poly-Si gate, the $O_3{\equiv}Si^+$ state may, together with protons, contribute to the positive charge.

There are several ways in which the formation of the $O_3{\equiv}Si{-}H$ defects in the oxide may occur. First, it may be generated by breaking Si–O and Si–Si bonds in the dual-moiety defect precursors $O_3{\equiv}Si{-}O{-}Si{\equiv}O_3$ and $O_3{\equiv}Si{-}Si{\equiv}O_3$, respectively, followed by hydrogen decoration. Taking into account that the density of SiOH-related electron traps (which would result from the Si–O–Si bridge rupture) appears to be considerably lower ($<5 \times 10^{11}$ cm^{-2} in sample B) than the density of E′ centres, this former process is unlikely to be involved in the oxide thermal degradation. However, there are indications that the rupture of the Si–O–Si bridges leading to generation of hydroxyls may happen at high irradiation doses [15]. Interaction of hydrogen with Si–Si links in SiO_2 has been suggested earlier to explain the dramatic increase in the E′ generation efficiency after wet etching of the silicon cover of the buried SiO_2 layer [10]. Taking into account that the presence of H-related species at levels $\sim$1 ppm is hardly avoidable during Si oxidation or anneal, the same process would lead to the formation of $O_3{\equiv}Si{-}H$ defects during oxide growth and post-oxidation anneal.

In conclusion, we found that the E′ centre observed after irradiation of SiO_2 layers thermally grown on Si is primarily in the neutral charge state when paramagnetic. Its efficient interaction with H and H_2 suggests that the neutral diamagnetic state is the H-passivated one. Therefore, we propose this centre to be similar to the E'_β defect in amorphous SiO_2. Involvement of both E′s and hydrogen in the positive charge trapping and generation of paramagnetic centres in the oxide leads to more complicated kinetics of positive charge trapping than the thus far favoured simple hole trapping by a E′ precursor site.

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