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DEFECT STATES AT THE SEMICONDUCTOR-INSULATOR INTERFACE: A CHEMICAL BONDING APPROACH

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This paper discusses the nature of the intrinsic bonding defects at the Si/SiO_2 interface, where three distinct defects P_b, N_{st} and Q_{ss}, have been identified through their different electronic properties. A possible local atomic environment for the Q_{ss} center is proposed. The final portion of the paper contrasts the bonding chemistry of oxides at interfaces with compound III-V semiconductors with the Si/SiO_2 interface.

I. Defects at the Si/SiO_2 Interface

In spite of extensive progress in device fabrication technology, residual defect densities of the order of 10^{11} cm^{-2} can be present in the immediate vicinity of a Si/SiO_2 interface. These defects have been classified phenomenologically through their electronic properties. Nishi[1] reported three esr signals at the Si/SiO_2 interface and designated them as P_a, P_b and P_c. Poindexter, Caplan and their co-workers[2,3] have shown that only one of these three, the P_b-center is an intrinsic bonding defect, a threefold-coordinated Si-atom, Si^{III}, with three Si-neighbors. The unpaired electron responsible for the esr signal, occupies a p-rich orbital that is normal to the interface for an oxidized [111] Si-face[2,3], and is canted, as expected on the basis of this assignment, for a [100] face[4,5]. Poindexter and co-workers further demonstrated: (i) that the densities of the P_b-centers and interface trapping states, N_{st}, behaved similarly with respect to various annealing and oxidation cycles, (ii) that the density of centers responsible for a fixed positive space charge within the oxide layers and designated as Q_{ss}[6] did not correlate with the systematic changes in P_b and N_{st}, and finally, (iii) that E'-centers, consisting of two neighboring Si^{III}, each with three oxygen neighbors and "sharing" a single and unpaired electron[7], were not observable; hence, their density was less than 10^{10} cm^{-2}. On the basis of (iii), they concluded that the E'-centers, which carry a net positive charge, could not be the main source of Q_{ss} which is generally in excess of 10^{11} cm^{-2}. This is not surprising since E'-centers are only observed in bulk a-SiO_2 following intense irradiation[7]. The correlated behavior of P_b and N_{st} suggests that these two defects may be associated with the same Si^{III} centers[2-5]. Finally, the lack of any correlation between Q_{ss} and P_b (or equivalently N_{st}) demonstrates that Q_{ss} is not related in any simple way to the P_b environment. This paper discusses a model for the Q_{ss} center, based on a threefold-coordinated and positively charged oxygen center, O^{III}, the so-called oxonium ion[8]. This proposal for Q_{ss} derives from a defect assignment for bulk a-SiO_2 in which the 604 cm^{-1} Raman line is assigned to the local cluster containing the O^{III} atom[9].

Recently there has been considerable interest in the nature of intrinsic bonding defects in both chalcogenide and oxide glasses. Well-annealed bulk chalcogenide glasses display no esr signals; however, an esr signal may be produced by optically pumping a sample held at low temperature[10]. Street and Mott[11], Mott, Davis and Street[12] and Kastner, Adler and Fritzshe[13] have shown that this behavior is explained by a model in which the intrinsic defects in these glasses are *oppositely charged pairs* of *over* and *under-coordinated* chalcogen atoms, so-called valence alternation pairs or VAP's. *Each* member of the pair has a spin-paired electron configuration, hence no dark esr. However, trapping of an optically-generated charged carrier at either member of the pair leads to a neutral center with an unpaired spin and hence the photo-induced esr. This defect model can be extended to a-SiO_2[9] wherein the corresponding bonding defects are onefold and threefold-coordinated oxygen atoms, C_1^- and C_3^+ in the notation developed by Kastner et al.[13]. One electron energy diagrams for these centers have been published elsewhere[9,14]. Referring to the shorthand notation for describing the defects, the letter signifies the atom species, C for chalcogen including oxygen (we shall later use T for a tetrahedrally-coordinated atom, Si); the subscript gives the coordination and the superscript the charge state relative to the *normal* bonding environment which is taken to be neutral. This charge state index is therefore a charge associated with the number of valence electrons in the particular configuration minus the charge associated with the valence electrons of the neutral atom. It is not the effective ionic charge of any particular atom, but is the integrated net charge in the immediate vicinity of a particular defect site. It is convenient to expand the notation and include in parenthesis the nature and number of the nearest neighbors. Hence, in a-SiO_2, where all bonds are assumed to be heteropolar in character, the normally-bonded oxygen is $C_2^\circ(2T)$ and the defects identified above are $C_1^-(1T)$ and $C_3^+(3T)$. In the $C_2^\circ(2T)$ configuration, four of the six valence electrons of the neutral oxygen atom are in non-bonding orbitals, and two electrons participate in covalent σ-bonding with the two silicon neighbors. The bond charge is displaced toward the oxygen atom giving the Si-O bond a partial ionic character; however, as discussed above, and in the spirit of the Mott-Street[11] and Kastner-Adler-Fritzshe[13] models, the charge superscript is taken to be zero. In the $C_1^-(1T)$ configuration the oxygen atom starts out with seven valence electrons ($2s^2 2p^5$) rather than six, so that the excess charge relative to the normal valence state is -1. One of the seven valence electrons is utilized in a covalent σ-bond with its neighboring silicon. The oxygen orbital in this bond is nominally pure p. The remaining six electrons go into non-bonding orbitals, two into a low-lying doubly occupied 2s-like state, and the remaining four into two higher lying and degenerate p-states with π-symmetry[14]. These $2p_\pi$ electrons enter into dative $d_\pi p_\pi$ bonds donating electron density to otherwise empty d-orbitals of the silicon neighbor[14]. Finally, the $C_3^+(3T)$ center starts out with five electrons; hence, the charge of +1. Two of these five electrons are non-bonding, whereas the remaining three enter into σ-bonds with the three silicon neighbors. The charge in these σ-bonds is displaced toward the oxygen atom, so that the net charge of +1 is distributed over the entire defect cluster consisting of the threefold-coordinated oxygen atom and its three silicon neighbors. The bonding geometry at this center is pyramidal with the oxygen atom at the apex and the three silicon atoms at the base[9,14].

Kastner et al.[13] pointed out that the formation of a charged-defect pair does not decrease the total number of covalent bonds, so that the energy for the creation of a defect pair is low (∿1-2eV) and consequently, the number of defect-pairs in a well-annealed glass could be high. For example, the number of defects, as estimated from an interpretation of weak features in the vibrational spectra of a-SiO_2 is $\sim10^{19}$ cm^{-3}[9]. Transport studies on a-SiO_2, in particular the scattering mechanism for the electron mobility, also suggests a similarly high density of neutral defect centers[15].

Greaves[16] has proposed an alternative model in which the defect pairs in a-SiO_2 are C_1^-(1T) and T_3^+(3C). Lucovsky[9] has argued against this model on two counts: (i) it requires the breaking of a heteropolar bond which has considerable covalent character and its replacement by a weaker ionic bond, and (ii) the Raman signature of a T_3^+(3C) center would consist of two-polarized defect modes, not the single mode which is observed.

The density of Q_{ss} defects in the vicinity of the Si/SiO_2 interface is typically of the order of 10^{11} cm^{-2}. Since these defects are distributed over a distance of approximately 100 Å, the volume density is of the order of 10^{17}/cm^3. We assume that the defect configuration is associated with an atomic configuration in which a single silicon or oxygen atom has a valence other than that required for the normal bonding in a-SiO_2. This gives two candidate defect configurations, T_3^+(3C) and C_3^+(3T). We have argued that T_3^+(3C) is not a characteristic bonding defect in a-SiO_2; however, experiments have shown that T_3^+(3C) centers can be formed following irradiation and that this center is a constituent of the E'-complex[7]. In contrast, C_3^+(3T) centers are present in pristine a-SiO_2 and their number increases upon irradiation as evidenced by the behavior of the 604 cm^{-1} Raman mode[9]. We have argued above that C_3^+(3T) centers occur in pairs with C_1^-(1T) so that their positive charge is compensated by their negatively charge partner. Hence, in order for the C_3^+(3T) center of a VAP to contribute to Q_{ss} the charge on the companion C_1^-(1T) must be injected in the crystalline Si substrate on which the oxide is grown, or into the metal layer of an MOS structure. This is not likely since the companion center, a C_1°(1T) has an unpaired spin[13] and would therefore contribute to an esr signal which is not observed. Alternatively, pair formation may not necessarily occur near the interface due to deviation from stoichiometry and C_3^+(3T) centers may be produced without their conjugate charged partner.

II. Oxide Formation of III-V Semiconductors

There is considerable interest in developing insulators that can be utilized in an MOS technology employing compound III-V semiconductor The materials receiving the most study have been GaAs and InP. Several different approaches have been explored, native oxides produced thermally, by anodization or plasma techniques, and non-native insulators including oxides and nitrides. The most success has been achieved for InP, where promising results are obtained using a-SiO_2 as the insulated gate layer[17]. In contrast any oxide formation on GaAs yields a relatively high density of interfacial defect states[17]. We wish to emphasize two aspects of native oxide formation which have a bearing on thes observations regarding the different behaviors of GaAs and InP.

G. Schwartz and his co-workers[18] have performed extensive studies of native oxide formation on III-V semiconductors. In particular, they have generated tenary phase diagrams relevant to oxidation of GaAs and GaP. We here assume that oxide formation on GaP and InP are qualitatively similar. For GaAs, the oxidation reaction can be written as

$$4\ GaAs + 3\ O_2 \longrightarrow 4\ As + 2\ Ga_2O_3\ , \qquad (1)$$

whereas for GaP and InP, the reaction is different and given by

$$GaP + 2O_2 \longrightarrow GaPO_4 \qquad (2)$$

In the first case there is a pile-up of As at the GaAs-Ga_2O_3 interface. This clearly degrades the electronic properties of the interface. For the case of GaP and InP, the oxide can be homogeneous and be viewed as a diatomic analog of SiO_2. Experiments on GaAs indicate an intermediate oxidation state in which Ga_2O_3 and As_2O_3 are both formed. For the case of native oxide formation on InP (or GaP) the oxide may be viewed as a mixture of In_2O_3 (or Ga_2O_3) and P_2O_5[19]. There is a significant difference in local bonding of a As_2O_3[20] and a-P_2O_5[21]. For a-As_2O_3 the As-atom is threefold-coordinated, with the fourth bonding position being occupied by a non-bonding pair, whereas in a-P_2O_5 each P-atom is fourfold-coordinated with three bridging oxygen atoms and one multi-bonded terminal oxygen atom[19]. This difference in local coordination at the As and P-atom sites in their oxides may well be the root of the significant differences in the equilibrium behaviors described in equations (1) and (2). It can also account for differences in the electronic behavior, wherein the non-bonding pair on the As-atom may act as a hole trap. In contrast, all of the bonding positions in a-SiO_2 are occupied by equivalent and bridging oxygen atoms[19]. The electronically active defects in a-SiO_2[9] and at Si/SiO_2 interfaces are then associated with either under-coordinated (dangling bonds) or over-coordinated atoms.

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