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1998 J. Phys.: Condens. Matter 10 89

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J. Phys.: Condens. Matter **10** (1998) 89–93. Printed in the UK PII: S0953-8984(98)87016-1

Positively charged bonded states of hydrogen at the (111)Si/SiO$_2$ interface

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Received 21 August 1997

Abstract. Annealing of thermal (111)Si/SiO$_2$ in hydrogen in the temperature range 450–800 °C is found to introduce a considerable density (up to 10^{13} cm^{-2}) of positively charged centres, ascribed to H bonding. However, there is no comparable density of dangling bonds initially present nor generated at the Si/SiO$_2$ interface that could account for the observed hydrogen bonding. The hydrogen is suggested to be trapped in the positively charged valence-alternation state—threefold-coordinated oxygen—resembling the well known hydronium ion $(H_3O)^+$. The activation energy of dissociation of this state was found to be about 2.4 eV.

Hydrogen represents an 'intrinsic impurity' at most of the solid interfaces, such as Si/SiO$_2$, because its presence is hardly avoidable during technological processing. Routinely, the interaction of H with the host atoms is considered either as a passivation of non-saturated (dangling) bonds originating from the interfacial mismatch, or as a rupture of energetically less favourable bonding configurations resulting, again, in passivated dangling bonds [1]. However, this scenario is not the only possible one: it was suggested a while ago [2–4] that the structural flexibility of the host network, e.g. an amorphous matrix, allows formation of intrinsic coordination defects, often designated as valence-alternation states [3]. The principal features of these states are the conservation of the total bond number in a solid and absence of dangling-bond states (the system remains diamagnetic). In the present article we will show that this approach is also applicable to the hydrogen bonding at the interface between a crystal and an amorphous solid. We found that exposure of thermally grown (111)Si/SiO$_2$ to hydrogen in the temperature range 475–800 °C results in the formation of a positive charge related to a bonded state of hydrogen without, however, rupture of the interfacial Si–Si or Si–O bonds. The inferred high binding energy of this state, about 2.4 eV, is ascribed to the threefold-coordinated oxygen centre, in which an ionized hydrogen (proton) is bonded to lone-pair electrons of an interfacial oxygen atom.

The samples studied were prepared by thermal oxidation of low-doped ($n_D, n_A < 5 \times 10^{14}$ cm^{-3}) n- and p-type (111) Si wafers in dry oxygen. Oxidations were performed either in a clean-room facility at 1000 °C, with subsequent annealing in N$_2$ for 30 min at the same temperature, or in a laboratory set-up at 970 °C, without any post-oxidation annealing. The oxide thickness was in the range 35–72 nm. After the oxidation, the Si wafers were cleaved into $\approx 1 \times 1$ cm^2 pieces, which, without any aqueous surface cleaning, were subjected to isochronal annealing in H$_2$ (1.1 atm, $\sim$1 h) in the temperature range 400–800 °C, terminated with fast cooling to room temperature (with an exponential temperature decay time constant of $\sim$200 s). The semitransparent Au or Al electrodes were evaporated onto the oxide employing a resistively heated source to form metal–oxide–semiconductor

0953-8984/98/010089+05$19.50 © 1998 IOP Publishing Ltd

(MOS) structures. The charge density at the interface was determined by monitoring the shift of the 1 MHz capacitance–voltage (C–V) curve. The density of dangling-bond states N_{it} at the (111)Si/SiO_2 interface was estimated from the shift of the C–V curve caused by the temperature lowering from 300 to 77 K; the latter induces a shift of the Fermi level at the Si surface leading to the recharging of the interface defects [5]. The results of these measurements were compared to the density of Si dangling bonds at the (111)Si/SiO_2 interface (P_b centres) determined by means of electron spin resonance (ESR) at $T = 4.2$ K as described previously [6]. The density of Si dangling bonds in the near-interfacial SiO_2 layer (E'_γ centres) was determined from ESR after hole injection into SiO_2 [7].

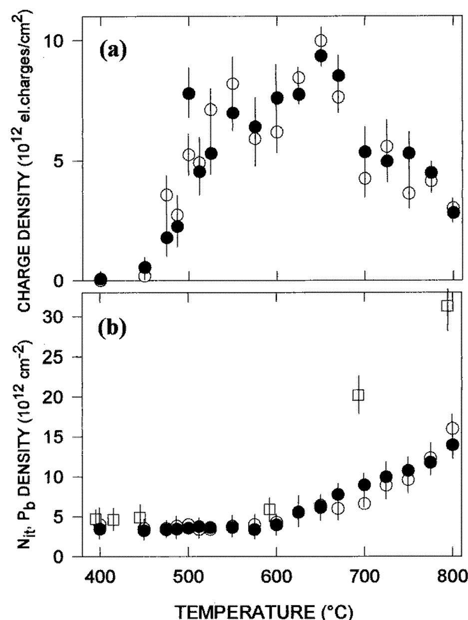

Figure 1. The density of positive charge as a function of the temperature of the annealing in H_2 (a) and of the density of Si dangling-bond defects (P_b centres) observed after subsequent depassivation (b) in clean-room-processed (111)Si/SiO_2 structures on n-type (full symbols) and p-type substrates (empty symbols). The open squares in (b) refer to the P_b-centre density determined by means of ESR.

The hydrogen annealing was found to produce a considerable density of positive charge in the Si/SiO_2 structures as shown in figure 1(a) as a function of the H_2 annealing temperature for the clean-room-processed samples; as-oxidized samples have a relatively low net charge density ($< 3 \times 10^{11}$ electronic charges cm^{-2}). Similar results were obtained for the samples oxidized in the laboratory facility. It is seen that from 450 °C onward, H_2 annealing produces positive charge approaching densities of $\sim 10^{13}$ electronic charges cm^{-2}. At $T > 670$ °C the charge density gradually decreases. Despite this high density of positively charged centres, we have not observed a related ESR signal, i.e., the hydrogen-induced positive charge is diamagnetic. The density of interface states in all of the samples subjected to H_2 annealing was found to be below 5×10^{10} cm^{-2}, which we attribute to the passivation of dangling-bond defects by hydrogen [8]. Subsequently, the samples were subjected to an additional depassivating anneal in a high vacuum ($< 4 \times 10^{-7}$ Torr, 620 °C, $\sim$1 h), resulting in complete elimination of the hydrogen-induced

positive charge. The density of interface states measured after this depassivation step is shown in figure 1(b). Nearly equal densities of interface states are observed in the n- and p-type samples, pointing to the symmetric character of the interface state distribution in the upper and lower part of the Si bandgap, as would be expected for P_b centres [1]. Indeed, the ESR results, also shown in figure 1(b), support the identification of the observed interface states as P_b centres. The somewhat lower density of the defects detected by electrical measurements is probably related to the partial Coulomb blockage which prevents the charging of all of the P_b states available at the interface during the C–V probing. The trends of the P_b behaviour are clear from figure 1(b): starting from the 'natural' density of Si dangling bonds of (4–5) $\times$ 10^{12} cm^{-2} determined during oxidation [6], it shows an increase from 580 °C onwards. Obviously, this temperature behaviour differs from that for the positive charge, shown in figure 1(a). Moreover, we found that the samples in which the density of P_b centres was intentionally varied using vacuum heat treatment as described previously [6], upon subsequent H_2 annealing exhibit a comparable density of positive charge to the as-oxidized samples. Also, we have not observed (within an accuracy of 20%) any increase in the hole trapping in SiO_2, which, in agreement with the literature [9], indicates that annealing in H_2 produces no oxygen vacancies in the oxide.

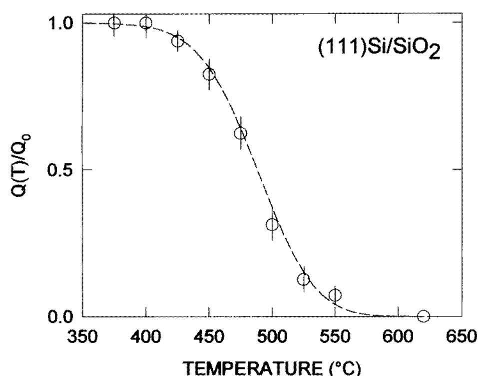

Figure 2. The isochronal annealing (vacuum, 1 h) of the positive charge, introduced by annealing in H_2 at 650 °C at the (111)Si/SiO$_2$ interface, plotted as the remaining fraction of charge versus the annealing temperature. The symbols represent the experimental points, while the line is the result of fitting first-order kinetics (see the text).

Repeated alternated anneals in H_2 at 650 °C and in vacuum at 620 °C reveal the charging process to be nearly reversible; some gradual decrease in charge density is observed with increasing number of annealing cycles, but this may be due to accumulated contamination of the oxide surface during metal electrode etch-off. This reversible annealing of the H-induced positive charge points to a relationship with some bonded state of hydrogen. To determine the binding energy of this state, the samples previously subjected to 650 °C H_2 were subsequently annealed for 1 h in vacuum in the temperature range from 375 to 620 °C. The fraction of remaining positive charge $Q(T)/Q_0$ is shown in figure 2 as a function of the vacuum annealing temperature. The fitting of the annealing behaviour using first-order kinetics yields a binding energy of hydrogen of 2.39 eV and the standard deviation of 0.07 eV if one adopts the pre-exponential factor $k = 1.2 \times 10^{12}$ s^{-1} inferred previously for the release of H from the H–Si≡Si$_3$ complex [8]. The latter approximation may be seen to be realistic when one takes into account that the same mass of liberated particles and the close activation energies of the two processes (2.6 eV for H dissociation from

H–Si≡Si_3 [6]). The binding energy of H and the dangling bonds of Si and O atoms in SiO_2 is approximately twice as large [10], i.e., the observed annealing behaviour of the positive charge cannot be associated with oxide defects.

To establish the spatial location of the positive charge we performed experiments on internal photoemission of electrons from Si into SiO_2 [11]. The main observations are:

(i) the positive charge cannot be neutralized by injecting up to 10^{17} electrons cm^{-2} for the electric field in SiO_2 in the range 0.1–5 MV cm^{-1};

(ii) the current–voltage characteristics of the photoemission (not shown) exhibit no distortion by the electric charge.

The latter observation indicates that the positive charge resides close to the Si/SiO_2 interface [11]. The upper limit of the distance of the charge from the Si substrate is comparable to the mean free path of an injected electron in SiO_2, i.e. about 3 nm [12]. The charge stability against neutralization indicates that the first energy level of an electron in the Coulomb potential well of the positively charged centre is energetically located above the bottom of the Si conduction band [13]. Hence, an electron in this level will tunnel into the Si substrate, thus maintaining positive charge in the oxide.

The above experimental observations may be summarized briefly as follows: the hydrogen produces a positively charged bonding state at the $(111)Si/SiO_2$ interface without any correlation with bond rupture. An interesting observation is that most of the charge build-up is observed in the temperature range above that of charge annealing (cf. figures 1(a) and 2). This seems to indicate that the density of positive charge is governed by an intricate balance between the production of atomic H in the Si/SiO_2 system and, perhaps, its dimerization. The detailed analysis of this balance is outside the scope of the present article. The important feature of the charging process is that the bonding of hydrogen occurs in a 'non-invasive' (non-bond-breaking) configuration which can be reversibly populated and depopulated. In the search for a possible explanation for such a bonding state, one may first recall the observation of de Nijs *et al* [14] that the hydrogen-induced donor interface states in irradiated (100)Si MOS structures appear to be stable when kept charged positively, in complete contrast with their neutral state. Also, there is the behaviour of H^+ in the bulk of the oxide, showing distinct annealing out at room temperature [14–16]. Such a sensitivity of the defect stability to the charge state together with the detection of H release during annealing led to a hypothesis that the state may represent an analogue of the well known hydronium ion (H_3O^+) at the Si/SiO_2 interface—that is, a Si–$(OH)^+$–Si complex [14]. A similar idea was employed to explain the creation of an oxonium ion by picking a H atom from the neighbouring passivated Si surface atom [17, 18], or oxonium creation by breaking the surface Si–Si links in the $Si/SiO_2/Si$ structures when subjected to high-temperature annealing followed by H_2 treatment [19]. However, both of the latter models predict the presence or generation of P_b centres, correlated with the density of positive charge. Our experimental data indicate that this is definitely not the case at the $(111)Si/SiO_2$ interface. Therefore, we consider the hydronium-like configuration suggested in reference [14] as most probable one. The stability of the positively charged state of hydrogen in defect-free SiO_2 is also supported by recent *ab initio* calculations [20].

There are, however, significant differences between the defects produced by irradiation and H_2 annealing. The radiation-induced states are unstable even at room temperature [14], while the positive charge found to be produced here by H_2 annealing is stable at 400 °C for hours (if atomic H is absent). The radiation-induced states have the energy levels of the neutral state distributed within the Si bandgap [14], while in the annealing-produced ones this level is shifted outside the Si bandgap. Thus, within the model of the

hydronium-like complex, one has to consider the possibility of some rearrangement; such a rearrangement may be understood by taking into account that the temperature range of the H-induced positive charging is close to the point of polymorphic transformation in SiO_2 (the α-quartz $\rightarrow$ β-quartz transition, $T = 573$ °C). An increase in the rate of rearrangement with temperature might then explain the increase in the charge density that occurs despite the simultaneous increase in the charge annealing rate.

In conclusion, we found that the exposure of thermally oxidized (111)Si to hydrogen in the temperature range 450–800 °C results in the generation of a positively charged state, characterized by an activation energy for annealing of about 2.4 eV. The state is diamagnetic and shows no correlation with the dangling-bond defects at the Si/SiO_2 interface. It probably represents the valence-alternation centre in SiO_2, i.e. threefold-coordinated oxygen. These observations may shed light on the problem of the nature of the fixed positive charge at the thermal SiO_2/Si interfaces, still unsolved after decades [21].

Acknowledgments

The authors are grateful to Dr J M M de Nijs (DIMES, TU Delft, the Netherlands) for providing the clean-room-processed samples.

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