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A unified microscopic mechanism for donor deactivation in Si

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Abstract

Dopant atoms segregate to $SiO_2/Si(001)$ interfaces. This causes problems during manufacture of submicron microelectronic devices. On the basis of ab initio calculations, we identify the mechanisms by which P atoms are bonded and deactivated under the interface. We argue that P segregation occurs by (1) trapping at interfacial dangling bonds, (2) trapping at vacancies and vacancy–oxygen complexes bound under the interface, and (3) formation of pairs of threefold-coordinated P atoms. The first mechanism is important at low dopant concentrations and when no vacancies are available, the second one dominates at medium dopant concentrations after P implantation, the third one controls the segregation at dopant concentrations around 10^{19} cm^{-3} or higher. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Si/SiO_2; Dopant deactivation; Dopant segregation

1. Introduction

Fabrication of silicon-integrated circuits involves implantation of a high concentration of donors. This is followed by processing at temperatures at which the dopants can migrate. CMOS technology relies on SiO_2 being placed next to doped regions of silicon. Segregation of dopants to SiO_2/Si interfaces causes a significant redistribution and deactivation of dopants, so that only a fraction of the dopant atoms remains electrically active [1]. As much as 50% of the implanted dopants can be lost during the pad oxide etch [2], and the interface can collect at least $3\times10^{14}/cm^2$ dopant atoms, that is, nearly a monolayer (1 ML $= 7\times10^{14}/cm^2$). Redistribution of the dopant atoms below gate oxides affects electrical parameters of MOS transistors. For example, the threshold voltage can be changed by 50% of its ideal value [3]. It is thus highly desirable to gain insight into the mechanisms for donor segregation and deactivation, since these effects will cause problems in the design and manufacture of ultra-sub-micron silicon devices.

In the literature, the segregation has been thus far treated at a phenomenological level. Details of dopant–interface interactions are unknown. It is unclear what causes the segregation, what are the atomic and electronic structures of the segregated donors, and what are their energies. A simple but physically correct description of the segregation mechanism would facilitate modeling of technological processes [1]. The purpose of this work is to provide fundamental insight into the physics of dopant segregation by ab initio studies of a typical donor, phosphorus.

The published segregation models [4–8] assume that the interface has a fixed number ($\sim$1 ML) of sites at which dopant atoms can be trapped, and do not differentiate between traps. However, this is inconsistent with the measured dependence of the dose loss on the implanted dose ("traps only", Fig. 1a). This inconsistency indicates that such models would fail when the dopant concentration changes strongly along the interface (as under oxide sidewalls in MOS transistors), even though these models work over a limited concentration range.

Here we formulate and discuss a general segregation model, based on results from ab initio calculations and

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Auger electron spectroscopy measurements. We verify the model using published secondary ion mass spectroscopy (SIMS) data on P segregation [2,7,9]. Our results highlight the importance of mechanical strain near the interface, which promotes double-trapping (pairing) of dopants. We show that, as a consequence of pairing, the segregation mechanisms for high- and low-doping levels are qualitatively different.

We briefly describe in the next section the calculation methods and microscopic models for the interface and traps. In Section 3 we present and discuss the segregation model, and summarize our results.

2. Microscopic models

The calculations were done by ab initio supercell approaches.[1] Interface structures were calculated with the fhi96md code [10]. The reliability of results was verified by comparison with optimized geometries, electronic structures, and energy differences for test silicon–oxygen and silicon–oxygen–phosphorus structures computed with other ab initio codes (full-potential LMTO code [11,12] and LCAO-based ab initio pseudopotential code [13]) and with energy differences obtained by a semi-empirical method applied to clusters of roughly the same size as the supercells. The bulk defect calculations were done by the LCAO-based ab initio pseudopotential code SIESTA [13], using large cells.

We estimate that the numerical accuracy for energy differences between two atomic geometries associated with the same interface model is ~0.2 eV per unit cell (see footnote 1). The accuracy of binding energies is ~0.2 eV per phosphorus atom bonded in a complex. The numerical error is dominated by k-point sampling, small distance between defects in the neighboring supercells (in the interface models), and the LDA band-gap problem. The latter affects energy differences and binding energies when defects with deactivated donor atoms are compared to a substitutional donor. A band-gap correction was employed in such cases.

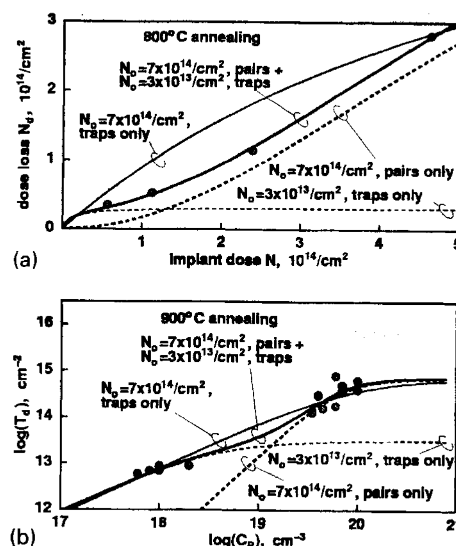

Fig. 1. Dopant pairing and dose loss: (Thin lines) trapping only, (Thick solid lines) pairing and trapping, (Broken lines) contributions from pairing (thick) and trapping (thin). (a) Dependence of P dose loss N_d on P implant dose N, SIMS data [2]. If traps only are assumed, the functional dependence is qualitatively wrong. Pairing and traps together give an excellent fit.(b) Dependence of P dose loss N_d on P concentration C_P close to the interface, SIMS data [9,7] The trap-dominated (low C_P) and pairing-dominated (high N_d) regimes are clearly visible.

The atomic geometries addressed in this work include (a) several models of the interface, (b) phosphorus atoms placed in various configurations at or near the interface, and (c) P atoms bonded in bulk-like defect complexes with and without oxygen. The details of these calculations will be given in a separate publication. Here, we focus on the hitherto unexpected effect of dopant pairing (that is, trapping of two P atoms at the same complex) below the interface.

The interfacial atomic structures were designed in such a way that as few atoms as possible represented the key features of the interface. These models were then systematically expanded towards increasingly realistic geometries. The fundamental geometry is built on the basis of a bulk Si(001) $1\times1\times8$ cell with two oxygen atoms inserted into Si–Si bonds in one of the (001) planes (Fig. 2a). The resulting SiOSi sandwich is stretched along the (001) axis to acommodate the compressive stress created by the insertion of oxygen. This makes a crude model of an amorphous SiO_2/Si(001) interface: each interfacial Si atom of the substrate has two O neighbors. There is no real SiO_2 in this system, but since phosphorus atoms are expelled from SiO_2 into silicon and since Si–O bonds are much stronger (stiffer) than Si–Si bonds, this numerically efficient model reasonably simulates an interface-like environment for exploratory

[1] Car-Parrinello type of pseudopotential calculations, with Local Density Approximation (LDA) after Ceperley and Alder [19] in the parameterization of Perdew and Zunger [20], and nonlocal pseudopotentials [21,22] in Kleinman-Bylander form [23]. Interface structures done by fhi96md code [10] in Si(001)-type supercells with lateral dimensions 2×2 to 4×4, typically six to eight Si layers and a single oxide layer with various boundary conditions described in the text. Convergence: 40 Ry cutoff for plane waves, tests between 16 Ry and 40 Ry; Brillouin zone sampled at the points equivalent to $(\frac{1}{4},\frac{1}{4})$ point of the fully symmetric 4×4 surface cell, test done at Γ and $(\frac{1}{4},\frac{1}{4})$ points from 4×4, 3×3, and 2×2 cells. Bulk defects with SIESTA [13] in FCC supercells based on a 128 Si bulk cell, double-zeta basis-set (tests with single-zeta).

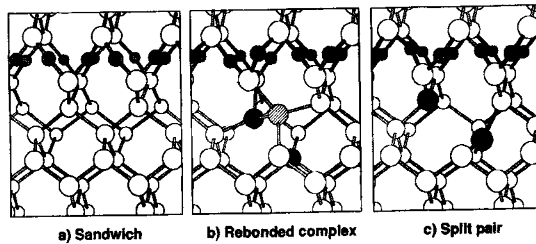

Fig. 2. Generic structures of phosphorus (black) trapped under SiO_2/Si(0 0 1). The phosphorus atoms of these P_2 complexes are deactivated (electrically neutral). (a) Idealized model of the SiO_2/Si(0 0 1) interface, (b) The dashed Si atom and its P neighbor form a pair of {1 1 3}-rebonded lattice atoms, (c) Threefold-coordinated P atoms of a distorted nearest-neighbor P_2 pair.

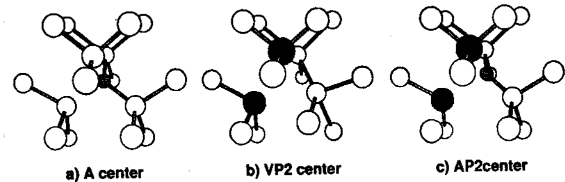

Fig. 3. Generic structures for phosphorus (black) trapped at vacancy defects in bulk Si. The phosphorus atoms of these P_2 complexes are deactivated (electrically neutral): (a) The oxygen(gray)-vacancy (V + O) neutral A-center, (b) The pair of P atoms trapped at a vacancy, (c) The pair of P atoms trapped at an A-center.

studies of the interaction between phosphorus, oxygen, and silicon atoms.

We found that at least two atomic configurations allow covering any SiO_2/Si(0 0 1) interface with nearly a full monolayer of P ($\sim 5 \times 10^{14}/cm^2$). (Fig. 2b and c). These structures involve no pre-existing defects, neither in Si nor in SiO_2/Si(0 0 1). Each of them is built on the basis of two threefold-coordinated, electrically neutral P atoms. One of these complexes (Fig. 2b) employs a local rearrangement of Si lattice bonds which we name "{1 1 3} rebonding" [14]. The geometry of {1 1 3}-rebonded atoms is analogous to the atomic configuration which is temporarily acquired near the barrier along the concerted-exchange path of Si self-diffusion [15]. The other structure is simply a distorted nearest-neighbor PP pair (Fig. 2c).

These complexes, in particular the PP pair, may be unstable in the bulk. But they are stabilized next to the interface, with the binding energy $\sim$0.5 eV/mole in intrinsic material and $\sim$1 eV/mole in n-type material. The stabilization takes place because the oxide helps to accommodate the stress caused by the deformation of the bonds around the defects and because the removal of a substrate bond makes the network more flexible, assisting in the relaxation of the interfacial stress.

In the bulk we found a stable complex between P and O in a P-decorated A-center (Fig. 3). The occurrence of the $V_{Si}P_{Si}$ complex (E-center) has been reported since a long time (donor trap) [16,17]. Pairing of P atoms has also been proposed at high doping levels. We found that in addition, in the presence of O atoms, the AP_2 complex is a strong candidate for double-trapping of donors. The complex is stable relative to various close associations of the component defects: the A-center (Fig. 3a) is stable relative to an interstitial oxygen O_i plus a vacancy V_{Si}, by $\sim$2 eV; and AP_2 (Fig. 3c) is stable relative to AP + P_{Si}, and to O_i + $V_{Si}P_2$ (Fig. 3b), by $\sim$0.5–1.3 eV. We thus find that two P donors and an O interstitial can lower their energy by ejecting a Si lattice atom to an interfacial step.

It is important to remark, however, that there are no PO bonds in the complex. The physical mechanism for P double-trapping and deactivation simple: through relaxation, each P atom assumes a three-fold coordination and re-traps an electron from the conduction band. This readily leads to a substantial energy gain, from electron-capture. There is also gain from exchanging the dimerized Si dangling bonds of the A-center (see Fig. 3) for the saturated inert lone-pairs of P (around $\sim$0.7 eV). The pairing is in this case also favorable, relative to the simple PP complex, because there is no significant stress build-up compared to an already existing A-center. Summarizing our results up to this point, we found that not only P atoms may be trapped at vacancies and A-centers, they can also pair at such defects.

Turning now to Si processing, implantation creates interstitials and vacancies. Many of these recombine shortly after the implanted ion rests in the substrate, but some vacancies escape recombination and migrate to the interface. Implantation also kicks out some oxygen atoms from the screen oxide into the subsurface, where they will combine with vacancies and form A-centers. Annealing may then, instead of activating the P atoms, bring them close to the traps where they will be deactivated (as E or AP centers, single-trapping). However, if there is a high concentration of phosphorus, pairing may take place. Pairing can then happen as PP complexes, or as stable $V_{Si}P_2$, AP_2, or {1 1 3} rebonded complexes.

3. Thermodynamical model

We now perform an analysis of published SIMS data, using a thermodynamical model to estimate the dependence of the segregated dose N_d on the concentration C_P of active phosphorus under the interface. For this purpose, we assume that: (1) N_o deactivation sites exist under the interface. (2) Dopant atoms can be deactivated by pairing or trapping. (3) The corresponding reaction constants are thermally activated. (4) The active and

inactive dopants under the interface are in quasi-equilibrium (meaning here that activation rates = deactivation rates). This leads to

$$N_d = \frac{N_o C_P^2}{C_P^2 + B^2 \exp(-2E_s/kT)}. \tag{1}$$

When segregation is dominated by pairing and to the usual

$$N_d = \frac{N_o C_P}{C_P + B \exp(-E_s/kT)} \tag{2}$$

when trapping dominates. As explained below, analysis of the literature data in terms of this simple model (Fig. 1) verifies the plausibility of the segregation mechanism proposed in this work. The $N_d(C_P)$ dependence is recovered for the whole dopant concentration range under the gate and sidewall oxides in MOS transistors.

The segregation energy due to pairing is ~0.4 eV/mole from Fig. 1 (800°C and 900°C) and from the data in Ref. [18] (1000°C, not shown), while the segregation energy due to trapping is ~1.3 eV. These values are close to our ab initio estimates for pairing and trapping of phosphorus at broken bond sites, respectively. The density of "deactivating sites" of N_o for pairing corresponds to a monolayer, while N_o for trapping is $\sim 3 \times 10^{13}/\text{cm}^2$, which is about 10 times more than the typical number of electrically active interfacial defects. This indicates that defects such as nonstoichiometric sites (Si–Si bridges) may act as dopant traps, or, as discussed earlier, some phosphorus atoms may be trapped by silicon vacancies and A-centers. In order to account for $\sim 3 \times 10^{13}/\text{cm}^2$ trapping sites (5% of a monolayer, or 0.05 ML), one needs approximately 0.01–0.02 ML vacant sites (each A-center can trap two, and each vacancy can trap up to four P atoms). Assuming that these vacancies are localized between one to five atomic layers below the interface, the volume concentration of the segregated vacancies must be around $5\text{–}1 \times 10^{20}\ \text{cm}^{-3}$. Calculations veryfying the stability of such a high vacancy concentration under SiO_2/Si(0 0 1) are in progress.

Our analysis indicates that any predictive simulation model which attempts to describe the segregation coefficient for P concentrations around $10^{18}\ \text{cm}^{-3}$ must account for the dopant pairing. The interface has much less than 1 ML of defect-related dopant traps, as expected of a high-quality boundary between two materials. The coexistence of pairing and trapping causes a two-regime dependence of the segregation coefficient on the implant dose (Fig. 1b). High- and low-coverage segregation are qualititatively different.

Concluding, we presented results of an ab initio study of dopant trapping and segregation to SiO_2/Si(0 0 1) interfaces. A simple and physically plausible model of the segregation of P atoms was formulated. We find that dopant segregation to the interface is aided by interfacial strain; so, segregation will also occur with any other dieletric that introduces strain. Moreover, losses at high implant doses are intrinsically nonlinear, because of pairing or double-trapping of dopants.

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References

[1] J. Dąbrowski, H.J. Müssig, M. Duane, S.T. Dunham, R. Goossens, H.-H. Vuong, Adv. Sol. State Phys. 38 (1999) 565.
[2] P.B. Griffin, S.W. Crowder, J.M. Knight, Appl. Phys. Lett. 67 (1995) 482.
[3] H.H. Vuong, C.S. Rafferty, S.A. Eshraghi, J.L. Lentz, P.M. Zeitzoff, M.R. Pinto, S.J. Hillenius, IEEE Trans. ED 43 (1996) 1144.
[4] M. Orlowski, Appl. Phys. Lett. 55 (1989) 1762.
[5] H. Sakamoto, S. Kumashiro, SISPAD (1997) 81.
[6] H.-H. Vuong, C.S. Rafferty, J.R. McMacken, J. Ning, S. Chaudhry, SISPAD (1997) 85.
[7] H.-H. Vuong, C.S. Rafferty, J. Ning, J.R. McMacken, J. McKinley, D.A. Stevie, SISPAD (1998) 380.
[8] R. Kasnavi, P.B. Griffin, J.D. Plummer, SISPAD (1998) 48.
[9] F. Lau, L. Mader, C. Mazure, Ch. Werner, M. Orlowski, Appl. Phys. A 49 (1989) 671.
[10] M. Bockstedte, A. Kley, J. Neugebauer, M. Scheffler, Comp. Phys. Commun. 107 (1997) 187.
[11] E. Bott, M. Methfessel, W. Krabs, P.C. Schmidt, J. Mat. Phys. 39 (1998).
[12] M. Methfessel, "NFP Manual", IHP Copyright, 1997.
[13] D. Sanchez-Portal, P. Ordejon, E. Artacho, J.M. Soler, Int. J. Quantum Chem. 65 (1997) 453.
[14] J. Dąbrowski, H.-J. Müssig, G. Wolff, S. Hinrich, Surf. Sci. 411 (1998) 54.
[15] K.C. Pandey, Phys. Rev. Lett. 57 (1986) 2287.
[16] G.D. Watkins, J.W. Corbett, Phys. Rev. 134 (1964) A1359.
[17] A. Fazzio, J.R. Leite, M.J. Caldas, Physica B 116 (1983) 90.
[18] Y. Sato, M. Watanabe, K. Imai, J. Electrochem. Soc. 140 (1993) 2679.
[19] D.M. Ceperley, B.J. Alder, Phys. Rev. Lett. 45 (1980) 567.
[20] J.P. Perdew, A. Zunger, Phys. Rev. B 23 (1981) 5048.
[21] D.R. Hamann, Phys. Rev. B 40 (1989) 2980.
[22] G.B. Bachelet, D.R. Hamann, M.A. Schlüter, Phys. Rev. B 26 (1982) 4199.
[23] L. Kleinman, D.M. Bylander, Phys. Rev. Lett. 48 (1982) 1425.