Control of Defect Concentrations within a Semiconductor through Adsorption

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The technologically useful properties of a crystalline solid depend upon the concentration of defects it contains. Here we show that defect concentrations as deep as 0.5 μm within a semiconductor can be profoundly influenced by gas adsorption. Self-diffusion rates within silicon show that nitrogen atoms adsorbed at less than 1% of a monolayer lead to defect concentrations that vary controllably over several orders of magnitude. The results show that previous measurements of diffusion and defect thermodynamics in semiconductors may have suffered from neglect of adsorption effects.

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Within semiconductors, native point defects such as vacancies and interstitial atoms mediate dopant diffusion [1] that is essential for making microelectronic devices [2]. Such defects also affect the performance of photoactive devices [3], the effectiveness of catalysts [4], the sensitivity of solid-state electrolyte sensors [5], and the efficiency of devices for converting sunlight to electrical power [6]. In this Letter, we show that defect concentrations as deep as 0.5 μm within a semiconductor can be varied controllably over several orders of magnitude through surface adsorption at less than 1% of a monolayer of nitrogen atoms. The results show that previous measurements of diffusion and defect thermodynamics in semiconductors may have suffered from neglect of adsorption effects.

Point defects mediate self-diffusion (including isotopes) within semiconductors [7], and the measured rate scales directly with the concentrations of these species. In strongly bonded solids such as silicon, the surface offers particularly efficient pathways for defect creation and annihilation because fewer bonds need to be broken than for bulk pathways [1]. Indeed, the capability of surfaces to create or destroy semiconductor defects is known from studies of surface morphology [8,9], silicon oxidation and nitridation [7], dopant diffusion for microelectronics [10,11], and metal oxide catalysis [12].

To demonstrate the influence of adsorption on the surface generation rate of defects, we measured self-diffusivities within silicon as a function of adsorbed nitrogen concentration on the surface situated roughly 0.5 μm away. Since the equilibrium concentrations of both vacancies and interstitials increase with temperature, heating typically produces a solid that is undersaturated (lower than equilibrium concentration) in both defect types, at least temporarily. The generation rate of these defects at the surface affects the degree of undersaturation and therefore the self-diffusion rate. More defects lead to proportionately faster diffusion. Our experiments were performed in an ultrahigh vacuum environment, so that adsorbate concentration could be controlled precisely to levels far below one monolayer. By contrast, the silicon self-diffusion measurements reported in the literature have been performed at atmospheric pressure. Even with inert gases, such environments typically contain low, ill-defined levels of reactive gases such as water or oxygen [10]. The effect of a Si surface that is atomically clean or has controlled, submonolayer adsorption has not previously been considered.

Our experiments employed a well-known isotopic heterostructure technique [13,14], in which a layer of silicon is grown epitaxially on Si substrates having a different ratio of the isotopes ^{28}Si and ^{30}Si. The concentration of ^{30}Si within the grown layer was 0.002%, compared to the natural abundance of 3.10% in the substrate. An easily measured step concentration profile of ^{30}Si thereby forms at the interface between the epitaxial layer and the substrate. Specimen samples [within 1° of the (100) orientation] were then briefly exposed to small amounts of gaseous NH_3 at 800 °C to produce monolayer to submonolayer levels of adsorbed nitrogen (without significant diffusion within the solid). The specimens were subsequently annealed for extended periods in ultrahigh vacuum to induce diffusional spreading of the initial ^{30}Si step in the absence of further adsorption. Further methodological details are available online [15]. After annealing, diffused ^{30}Si profile shapes were measured *ex situ* with secondary ion mass spectroscopy (SIMS), using a PHI TRIFT III instrument with a cesium ion beam.

Figure 1(a) shows an example series of the resulting SIMS profiles. The concentration of adsorbed nitrogen varied between zero and 3 monolayers (ML). The diffusion profiles differ substantially, and exhibit the most spreading for the atomically clean surface. Surprisingly, a concentration of only 0.01 ML substantially reduces spreading. The differences in the profiles extend down to the heterojunction interface, which is nearly 0.5 μm from the surface.

Self-diffusion in silicon involves diffusion of interstitials and vacancies, whose relative contributions have been the subject of considerable debate [13,14]. In Fig. 1(a), some

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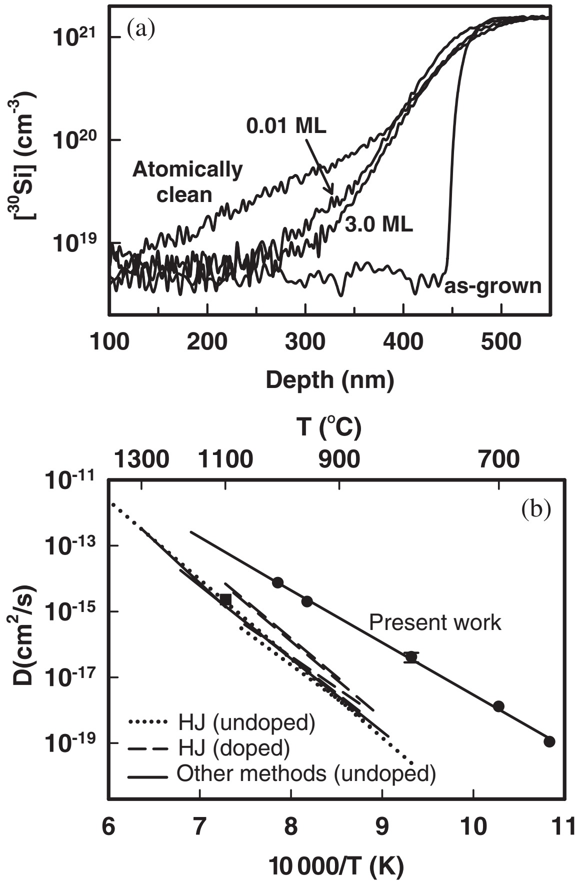

FIG. 1. (a) Profiles of ^{30}Si in isotopic heterostructures. Depth is measured with respect to the surface. Specimens (other than as-grown) supported various coverages of N, and were heated at 1100 °C for 60 min. (b) Self-diffusion coefficients in n-doped Si for the atomically clean (100) surface (●) compared with literature reports [13,14,18–22] with various methods and doping levels. HJ refers to heterojunction method. The square symbol (■) at 1100 °C corresponds to two overlapping points at 1 and 3 ML of adsorbed N, and lies within the range of previously published work.

profiles have nonerror function shapes that directly manifest the presence of a highly mobile defect species that periodically exchanges with the lattice [16]—interstitial atoms being a likely candidate. All profiles were analyzed by numerical simulation of combined defect hopping and exchange [15,17] to obtain the effective diffusion coefficient D that describes the ^{30}Si profile spreading observed in SIMS.

Figure 1(b) shows the temperature dependence of D for the atomically clean surface. Our numbers are 2 to 4 orders of magnitude larger than those reported in previously published work [13,14,18–22] done under less controlled adsorption conditions, and imply a correspondingly larger defect concentration caused by the surface. We obtain an activation energy of 3.12 ± 0.05 eV and a preexponential factor of 0.01 cm^2/s. The activation energy falls well below the published values of 4.0 to 5.0 eV. The magnitude of D observed here corresponds roughly to that of Bracht *et al.* [23] for radiation-enhanced diffusion, though the significance of this correspondence is unclear.

Doping type and level affects D in silicon due to the interaction of charged defects with the Fermi level [1,7]. This effect accounts for much of the spread in the literature reports shown in Fig. 1(b). However, our measurements (for n-doped Si) fall far outside the range of all these measurements, so that doping effects can be excluded as the primary cause. Furthermore, Fig. 1(b) shows overlapping data points measured with 1 and 3 ML of adsorbed nitrogen present ($D = 2.5 \times 10^{-15}$ and 2.3×10^{-15} cm^2/s, respectively). The points fall nearly 2 orders of magnitude below our clean surface results, and lie squarely in the midrange of previously published data. This agreement suggests that there was significant surface adsorption in past studies [13,14,18–22]. The value at 0.01 ML (3.5×10^{-15} cm^2/s) was only slightly higher than at 1 and 3 ML. The similarity of the results down to low coverages, coupled with the fact that adsorption was complete before diffusive spreading began, indicates that the results were not affected by vacancy injection into the solid that occurs during the formation of Si_3N_4 from ammonia [7].

These results are important because solid-state diffusivities find widespread application for modeling semiconductor behavior, and have long been used to estimate formation energies of native point defects. The strong bonding within semiconductors magnifies the importance of the surface in enabling the solid to reach an equilibrium concentration of defects. If defect exchange with the surface is slow, very long periods may be required to reach equilibrium. Thus, the results have important consequences for measuring both solid-phase diffusion coefficients and defect thermodynamics in semiconductors. Nonequilibrium phenomena may affect many previous experimental numbers that did not account for adsorption. For example, the measured activation energy for spreading represents the sum of the defect site-to-site hopping energy and a second energy assumed to equal the thermodynamic formation energy. With a passivated surface, most interstitials and vacancies must be created pairwise from within the bulk. The measured "thermodynamic formation energy" may actually represent a kinetic activation barrier for defect formation.

Most experimental and computational literature points to a formation energy between roughly 3.2 and 3.8 eV for both interstitials and vacancies in silicon [24,25], although numbers between 2.0 and 2.5 eV have been propounded [26,27]. Our results support these lower numbers. For example, if the key defect is the interstitial with a hopping energy of 0.72 eV [28], our data yield a formation energy of 2.4 eV. If the key defect is a vacancy with a hopping energy of 1.8 eV, as recently reported for this temperature range [23], our data yield a formation energy of 1.3 eV.

To demonstrate the influence of adsorption on the surface annihilation rate of defects, we measured ^{30}Si diffusion rates as a function of adsorbed nitrogen concentration under conditions of interstitial supersaturation (higher than equilibrium concentration), where the excess of interstitials was produced by ion implantation. The isotopic heterostructures described previously were implanted (energy $= 1$ keV, fluence $= 1 \times 10^{15}$ cm^{-2}) in ultrahigh vacuum with ^{30}Si to a depth much less than that of the heterostructure interface. Further methodological details are available online [15]. Subsequent annealing induced spreading of the implanted profile, mediated by excess interstitial atoms of both ^{30}Si and ^{28}Si, liberated continually from interstitial clusters that form in solid Si after Si implantation [11].

Figure 2 shows ^{30}Si profile spreading data, with nitrogen coverages varying from 0 to 1.2 ML. The profiles exhibit remarkable differences. Spreading from the as-implanted profile is almost negligible for the atomically clean surface, implying a very low background interstitial concentration relative to the other profiles. The effects of nitrogen adsorption show up at extremely low coverages down to 0.004 ML. Profiles between 0.01 and 1.0 ML could be superimposed exactly upon each other. At 1.2 ML, spreading increases further, but then remains constant up to 2.5 ML (the maximum examined here).

In implanted silicon, self-diffusion behavior is determined primarily by the interplay between migration of lone interstitials, annihilation at the surface, exchange of interstitials with lattice atoms, and exchange with interstitial clusters. The presence of spatially varying concentrations of interstitial clusters leads to interstitial concentrations that vary more strongly across the profiles than for unimplanted specimens. Thus, quantitative comparison of the annihilation rates at different adsorption levels is best done through the surface annihilation probability S rather than a single parameterized diffusivity. The SIMS profiles were analyzed by maximum likelihood estimation [29] to determine S for interstitials as a function of adsorbed nitrogen concentration. The model for these interactions was implemented [15] using the simulator FLOOPS 2000 [30], with key rate expressions and rate parameters described in detail elsewhere [28]. A typical profile fit appears in Fig. 2 for 1.2 ML. Figure 3 shows the values of S derived this way. S varies from 0.05 on the clean surface to 0.0003 above 1 ML. Most of the decrease (nearly 2 orders of magnitude) occurs between 0 and 0.01 ML.

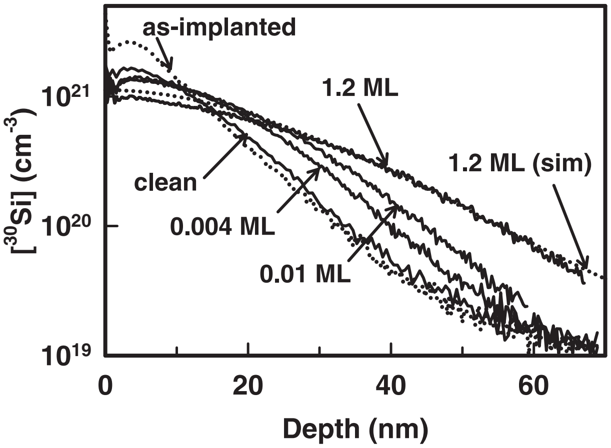

FIG. 2. Profiles of implanted ^{30}Si in p-type Si. Specimens (other than as-implanted) supported various coverages of N, and were heated at 980 °C for 90 min (except for the atomically clean surface, which was heated at 1000 °C for 120 min). About 20% of the total implanted ^{30}Si disappears altogether, presumably migrated to the surface, where SIMS cannot make reliable concentration measurements.

The results shown here for implanted material are important because the experiments simulate in many ways the technological implantation of dopants in Si to make pn junctions for microelectronic devices. Annealing of the implanted Si is employed universally to remove implantation damage, and the resulting profile shape plays a central role in device performance. It has not been recognized that surface adsorption can affect the profile shape so strongly. Adsorption avoids potential problems such as implantation damage and foreign atom incorporation that affect other forms of defect control for device manufacture [31].

The strong effects of adsorption on defect generation and annihilation should generalize to other semiconductors, where the formation rates within the solid are low so that surfaces could play a critical role. Since defect manipulation in most applications focuses on regions close to surfaces, manipulation through adsorption has particular practical relevance. The surface effects extend down to at least 0.5 μm, and may go much further for pure, high-quality solids in high-performance electronic, optical, and energy conversion devices where there are few mechanisms for defect exchange with the lattice or with defect clusters.

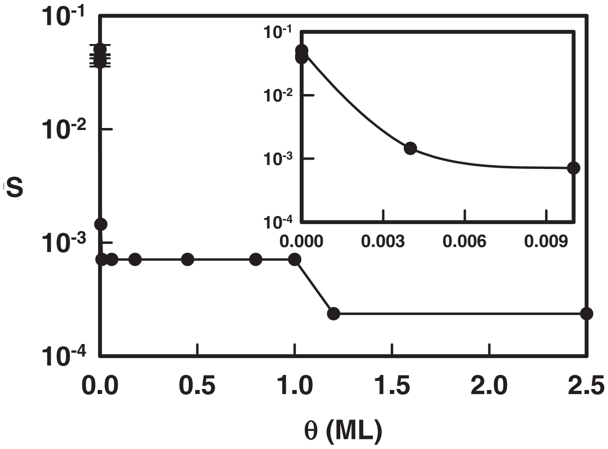

FIG. 3. Dependence of surface annihilation probability on N coverage. For clarity, the inset diagram reproduces data at very small coverages.

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