Nonthermal Effects of Photon Illumination on Surface Diffusion

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Nonthermal influences of photon illumination on surface diffusion at high temperatures have been measured experimentally for the first time. Activation energies and preexponential factors for diffusion of germanium and indium on silicon change substantially in response to illumination by photons having energies greater than the substrate band gap. Results depend on doping type. Ionization of surface vacancies by photogenerated charge carriers seems to play a key role. The results have significant implications for aspects of microelectronics fabrication governed by surface mobility. [S0031-9007(98)06842-2]

Diffusion on surfaces governs several process steps in microelectronics fabrication, including the formation of hemispherical grained silicon (HSG) for use in memory devices [1] as well as the filling of channels with metals for device interconnection purposes [2]. However, concomitant diffusion within bulk induces unwanted interface degradation and dopant migration in heterostructures. As a means to avoid these undesired processes, current methodology in microelectronics fabrication attempts to use low processing temperatures whenever possible. Consequently, interest has grown in nonthermal methods of modifying surface diffusivities. Photon illumination may represent one such technique, although this idea remains speculative.

Some work on electron-stimulated disordering [3,4] has indirectly hinted that photon illumination can enhance mobility [4]. However, the idea was left in embryonic form. We have independently postulated effects mediated by an interaction between charged vacancies or adatoms and illumination-induced variations in the surface Fermi energy [5,6]. However, up to now, no direct experimental evidence has materialized to back these ideas.

This paper fills the gap by presenting the first direct experimental evidence for photon-influenced surface diffusion at high temperatures. We have employed Ge and In on Si mainly as model systems whose thermal diffusion is reasonably well understood [6,7]. However, surface diffusion in the Ge-Si system also plays a role in emerging deposition technologies for novel heterostructure devices as well [8].

Surface diffusion was measured in ultrahigh vacuum via second harmonic microscopy [5–7]. This method images directly the temporal evolution of a one-dimensional step concentration profile, which in turn is created with a molecular beam and retractable mask. Illumination of the profile with a pulsed Nd:YAG laser at 1064 nm produces a small yield of surface second harmonic generation in reflection that varies with adsorbate concentration and therefore with position on the surface. Independent calibrations of yield vs concentration via Auger electron spectroscopy [6,7] permit direct conversion of raw second harmonic profiles into concentration profiles. Subsequent imaging processing [6,7], followed by a straightforward Boltzmann-Matano analysis [5], then yields the dependence of the surface diffusion coefficient D on coverage θ without parametrization. Control experiments in the present work showed that imaging itself did not perturb the profiles.

Experiments were performed on atomically clean Si(111), employing both n-type (As-doped, 8×10^{17} cm^{-3}) and p-type (B-doped, 1×10^{18} cm^{-3}) material. Arrhenius plots (Fig. 1) of the measured diffusivities under purely thermal conditions yielded diffusional activation energies E_{diff} and preexponential factors D_0 (Table I) which remained independent of doping type. The data matched our previously published work [6,7] within experimental error. However, illumination with a continuous-wave He-Ne laser produced a family of convergent Arrhenius plots (Fig. 1), with D rising for n-type doping and falling for p type. Control experiments with He-Ne illumination near the substrate thermocouple revealed no significant temperature increase. Diffusion was measured for coverages up to 0.6. D remained independent of θ in this range, in accord with thermal results [6,7]. Figure 2 shows for In how the change in Arrhenius parameters varied smoothly with intensity, in equal and opposite directions for the two kinds of doping. Table I encapsulates similar behavior for Ge. At a given intensity, the change in Arrhenius parameters remained independent of adsorbate, despite differences in the thermal parameters. Figure 2 also indicates that broadband radiation provoked changes identical to those of monochromatic radiation, provided that only photons having energies $h\nu$ greater than the band gap energy E_g of Si were included in the calculation of intensity.

The Arrhenius plots of Fig. 1 highlight another curious feature of the Ge data under illumination: The plots merged with the thermal data at sufficiently high temperatures. That is, E_{diff} and D_0 took on thermal values in this regime [9]. Low-energy electron diffraction (LEED)
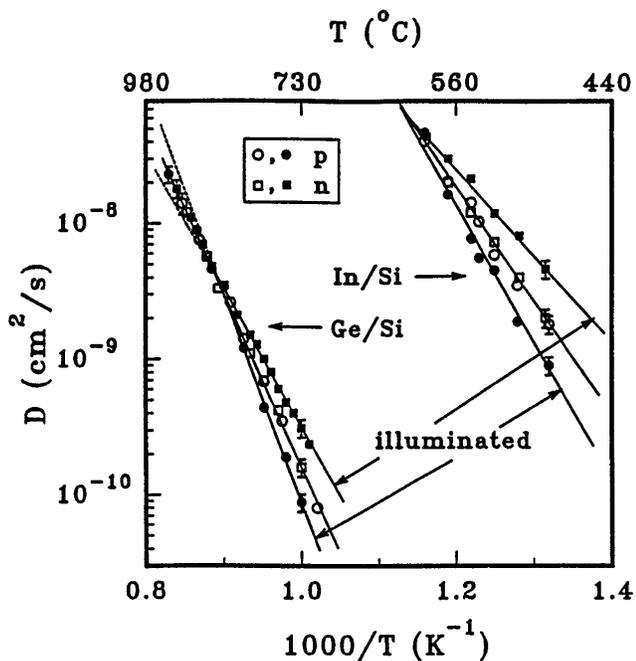
FIG. 1. Arrhenius plots for Ge and In diffusion at 1.9 W/cm² illumination intensity. Dashed lines for Ge represent extrapolations of low-temperature data for illuminated material in order to highlight the change in slope.

FIG. 2. Variation of diffusion parameters with illumination intensity and doping type for In. Illumination with a He-Ne laser (632.8 nm) and a broadband Xe arc lamp yielded identical results.

patterns near the isokinetic temperature revealed a gradual transition from 7×7 symmetry near 1060 K to 1×1 symmetry near 1110 K. This transition mirrors that reported for pristine Si(111) [10], but takes place at slightly lower temperatures in the presence of Ge.

Certain features of our results yield to straightforward interpretation. The influence of doping type and the importance of the condition $h\nu > E_g$ point to a driving mechanism that is electronic rather than vibrational. Quantitative analysis requires examination of what our experiment really measures: the mass transfer diffusivity D_M. This quantity comprises the product of the more well-known intrinsic diffusivity D_{int} and the fractional coverage θ of mobile adatoms [11]:

$$D_M = \theta D_{\text{int}}. \tag{1}$$

The distinction between D_M and D_{int} is important because in our experiments θ falls far below the nominal adsorbate coverage. On Si(111), adsorbates such as Ge and In substitute for surface Si atoms so that most adsorbate is rendered essentially immobile [5,7,11,12]. Molecular dynamics simulations have shown [7,13] that diffusional motion takes place via the formation of adatom-vacancy pairs, in close analogy to vacancy diffusion in the bulk. In a conventional thermodynamic framework, the measured values for E_{diff} and D_0 therefore contain contributions from the enthalpies and entropies of adatom-vacancy pair formation as well as those of intrinsic adatom motion. Thus, photon illumination can, in principle, affect either or both of the intrinsic and adatom-vacancy contributions.

Our data show that illumination increases E_{diff} by up to 0.3 eV on p-type Si and decreases E_{diff} by the same amount on n type, for a total swing of 0.6 eV. For Ge on Si, the entire intrinsic migration energy is only about 0.6 eV [7], suggesting that most of the observed effects originate from vacancies. Furthermore, the insensitivity of the photon-induced changes to an adsorbate type points to an underlying commonality, presumably vacancies on the Si surface.

The vacancy contribution to mass transfer diffusion through θ implicitly includes the charge state of the vacancy. In the bulk, Si vacancies take on charge states ranging from $+1$ to -2 [14]. Effects of vacancy ionization on bulk diffusion are well documented, with D_M obeying [14]

$$D_M = ([V^+] + [V^x] + [V^-] + [V^{2-}])D_{0,\text{int}}$$
$$\times \exp(-E_{\text{diff,int}}/kT), \tag{2}$$

where the subscript "int" refers to intrinsic diffusion. Each vacancy concentration $[V^j]$ varies as $\exp(-\Delta G_I^i/kT)$,

TABLE I. Surface diffusion parameters on Si(111).

Adsorbate	Doping type	E_{diff}(eV)		D_0(cm²/s)	
		Thermal	Illuminated[a]	Thermal	Illuminated[a]
Ge	n	2.44 ± 0.07	2.20 ± 0.07	$4 \times 10^{2\pm0.5}$	$3 \times 10^{1\pm10.5}$
	p	2.44 ± 0.07	2.71 ± 0.07	$4 \times 10^{2\pm0.5}$	$4 \times 10^{3\pm0.5}$
In	n	1.78 ± 0.04	1.48 ± 0.04	$1 \times 10^{3\pm0.4}$	$4 \times 10^{1\pm0.4}$
	p	1.78 ± 0.04	2.10 ± 0.04	$1 \times 10^{3\pm0.4}$	$4 \times 10^{4\pm0.4}$

[a]Below 1130 K. Illumination with He-Ne laser at 1.9 W/cm².

where ΔG_I denotes the free energy of ionization. Since charge transfer between the Fermi energy E_f and a vacancy level is required for ionization, the relative populations of differing charge states depend on the energy difference between E_f and these levels, and therefore on doping type and concentration. Although, to our knowledge, the charge states available to a vacancy on Si(111)-(7 × 7) remain unknown, significant evidence exists that an equation analogous to Eq. (2) governs surface diffusion as well [6].

For the Ge/Si system, the similarity in temperatures for the convergence of the Arrhenius plots and the disappearance of the 7 × 7 surface reconstruction argues for the importance of ionization effects. Thermal diffusion parameters remain invariant as the surface transforms from 7 × 7 to 1 × 1 at high temperature, suggesting that long-range order by itself plays no important role. The insensitivity of In diffusion to surface concentration [6] confirms this notion, as In/Si(111) passes through several reconstructions as the concentration increases [15] with no visible effect on D. Thus, the photon-induced effects seem to require some other governing process. Interestingly, *ab initio* calculations show that the 7 × 7 reconstruction of clean Si supports much larger separations of charge than does the 1 × 1, up to the equivalent of nearly one full electron [16]. Defect structures on Si(111)-(7 × 7) have been investigated only recently, but calculations for intrinsic Si indicate that each dangling bond of a vacancy supports roughly two-thirds of the charge density of the corresponding filled-site dangling bond [17]. Presumably, this number varies with the availability of charge carriers.

Equation (2) predicts that purely thermal diffusion should not vary with doping type if we assume that the surface Fermi level E_f remains pinned at the same location near midgap for both n- and p-type material. Near-midgap pinning for Si(111)-(7 × 7) has indeed been reported for undoped material at room temperature [18]. For the 2 × 1 reconstruction, the pinning position remains independent of substrate doping [19], making this independence plausible for 7 × 7. No studies of high-temperature pinning exist to our knowledge for Si(111), but for Si(100)-(2 × 1) the pinning level remains constant to within 0.1 eV up to 1200 K [20]. Hence, under dark conditions, the electronic occupation of energy levels should remain independent of bulk doping type. Equation (2) then predicts an invariance of thermal diffusivities with doping, in accord with our observations.

Clearly, the simple thermodynamic framework underlying Eq. (2) provides a useful perspective for explaining many of our results. However, Eq. (2) falls short in one respect: the decrease of D_M for p-type material. To see why, consider the electronic band characteristics of the Si in our experiments. Schematic diagrams of the near-surface electronic band behavior appear in Fig. 3. In addition to the assumption of near-midgap pinning, these diagrams also draw on the assumption that electronic occupancy within the conduction and valence bands near the surface obeys a description incorporating quasi-Fermi levels within the so-called "thermionic" limit [23,24]. Photogenerated electrons and holes in semiconductors thermalize rapidly within the conduction and valence bands, respectively. This quasithermalization splits the Fermi level into two quasi-Fermi levels [25] which define the electron and hole concentrations within these bands. The thermionic limit requires that the quasi-Fermi levels remain far from the band edges and that the drift velocity (v_d) of carriers in the surface space-charge region greatly exceeds the surface recombination velocity (v_r) [23,24]. Here we calculate that $v_d \sim 1000 v_r$, justifying the use of the thermionic limit.

Figure 3 shows that illumination renders the surface of n-type material essentially p type and vice versa. While Fig. 3 is sketched based on quantitative calculations, this conclusion holds regardless of the exact numbers employed for carrier recombination time, photon flux, absorption efficiency, etc. The result makes intuitive sense because the band bending for n-type material sweeps holes toward the surface and vice versa. However, as we intimated above, the implications this fact should have for D_M through Eq. (2) are not observed. In particular, a problem crops up concerning the decrease in D_M for illuminated p-type material. Molecular dynamics simulations of Ge surface diffusion on Si(111)-(1 × 1) extrapolate nearly perfectly over experimental data on the 7 × 7 surface [7]. These simulations incorporate no effects of ionic charge. While the correspondence may be coincidental, it suggests that the vacancies (and adatoms) responsible for thermal diffusion on 7 × 7 remain uncharged. In general, the population of uncharged vacancies remains invariant with changes in the Fermi level position [14]. Thus, if

n-type   p-type
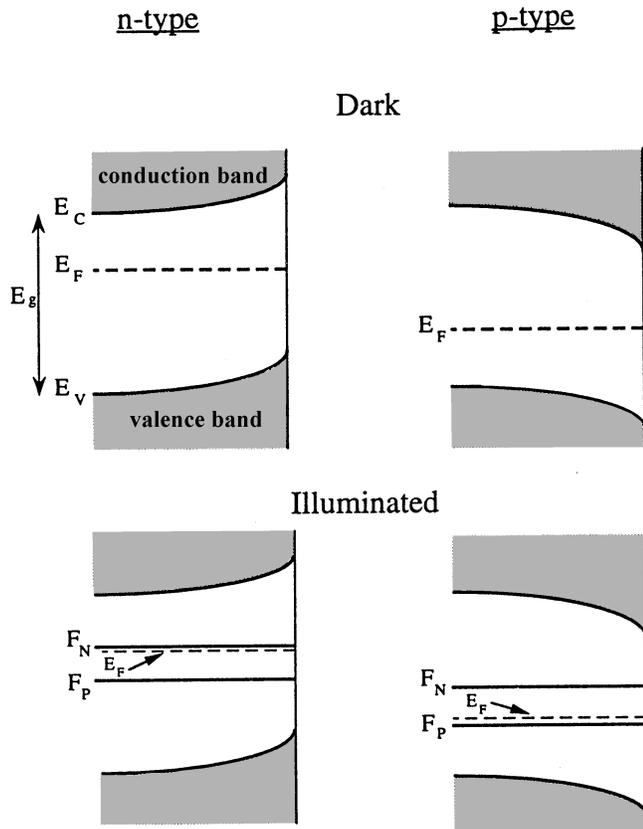
Dark

FIG. 3. Proposed near-surface band diagrams for dark and illuminated conditions on n- and p-type Si. In the dark, pinning of the surface Fermi energy, E_f near midgap induces the conduction band minimum E_c and valence band maximum E_v to bend near the surface. E_f itself remains constant throughout the semiconductor. Under illumination in the thermionic limit, quasi-Fermi levels F_n and F_p for electrons and holes split from E_f, but remain constant with respect to vacuum throughout the semiconductor. Positions of E_f, F_n, and F_p are drawn to scale according to calculations employing standard theory for photon absorption [21,22] under the conditions of our experiment. Photoreflectance measurements show [22] that at these temperatures illumination of itself does not change the band bending because the thermal carrier flux to the surface greatly exceeds the photogenerated flux.

illumination forms charged vacancies, Eq. (2) indicates that these extra species must increase D_M. However, for p-type material below 1100 K, D_M decreases in response to illumination.

Of course, arguing within the framework embodied by quasi-Fermi levels assumes some sort of thermalization of carriers among vacancy levels lying deep within the band gap—a questionable assumption. The potential difference across the space-charge region imparts considerable energy to the carriers accelerated through it. The details of carrier recombination at surfaces remain incompletely understood at present, but it seems plausible that, before recombining, these nonthermal carriers may interact with surface vacancies in a way that significantly alters their ionization states.

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