Unusually Low Surface-Recombination Velocity on Silicon and Germanium Surfaces

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We have found that a standard, widespread, chemical-preparation method for silicon, oxidation followed by an HF etch, results in a surface which from an electronic point of view is remarkably *inactive*. With preparation in this manner, the surface-recombination velocity on Si⟨111⟩ is only 0.25 cm/sec, which is the lowest value ever reported for any semiconductor. Multiple-internal-reflection infrared spectroscopy shows that the surface appears to be covered by covalent Si-H bonds, leaving virtually no surface dangling bonds to act as recombinatiuon centers. These results have implications for the ultimate efficiency of silicon solar cells.

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In the past decade semiconductor surface science has successfully studied the electronic structure and reconstructions of totally bare semiconductor surfaces. Recently, experimentalists have begun to assume a more active role[1,2] in modifying surface chemical structures to passivate the surface, i.e., to render the surface states electronically inactive. We can expect that this work will evolve more and more toward the artificial synthesis of surface chemical-bonding structures with desired physical properties. From the point of view of electronics, it is desirable to covalently satisfy *all* surface bonds, thereby shifting the surface states out of the band gap and into the valence and conduction bands.

We have discovered that a most commonplace surface-preparation method for silicon produces a surface whose electronic properties are very close to ideal from the point of view of electron-hole recombination. The preparation method consists of two steps: (i) the oxidation of the silicon surface and (ii) the dissolution of the oxide layer by hydrofluoric acid. (The oxidation can be produced chemically, thermally, or as a native oxide with similarly favorable results. We have generally preferred chemical oxidation in hot sulfuric acid.)

We employ an apparatus which makes contactless, *in situ* surface electronic measurements both in aqueous media as well as in vacuum. The experimental setup, shown in the inset of Fig. 1, resembles one[3] which performs contactless measurements of minority-carrier lifetime in silicon wafers. A strobe lamp injects carriers into the semiconductor wafer and the carrier-density decay is then monitored by an inductively coupled rf bridge. When the sample thickness L is sufficiently small, the decay of excess bulk-carrier density n_b is simply the sum of a bulk and a surface term[4]:

$$dn_b/dt = -(\tau_b^{-1} + 2S/L)\,n_b, \tag{1}$$

where τ_b is the bulk-minority carrier lifetime, S is the surface-recombination velocity (SRV), and the factor 2 accounts for the front and back surfaces. The reciprocal of the quantity in brackets was called by Shockley[4] the "filament lifetime" τ, which in general may depend on n_b. Notwithstanding the variable absorption depth of the white strobe-light source, the injected carrier density n_b will become spatially uniform and Eq. (1) will be correct provided that $L \ll (D\tau)^{1/2}$, where D is the ambipolar diffusion constant and $(D\tau)^{1/2}$ is the diffusion length.

Figure 1 is a semilog plot of the density decay from a 250-μm-thick Si⟨111⟩ wafer of a particularly high-quality boule of float-zone silicon. Notice that the initial decay rate at the highest injection levels is faster due to Auger recombination. By measuring the τ as a function of sample thickness and injection level, the bulk and surface contributions at a given injection level in Eq. (1) can be distinguished. An example of this is shown in Fig. 2. For the sake of self-consistency, the various thicknesses are all derived by etching down one and the same sample and the thickness ratios are precisely determined by sample weight.

The availability of such a simple method for diminishing surface recombination made it possible to rapidly screen samples from numerous batches of commercial float-zone silicon until a batch with particularly long bulk lifetime was found. For perspective, the lifetime of 35 msec is about 20 times better than the commercial specifications and about 1000 times better

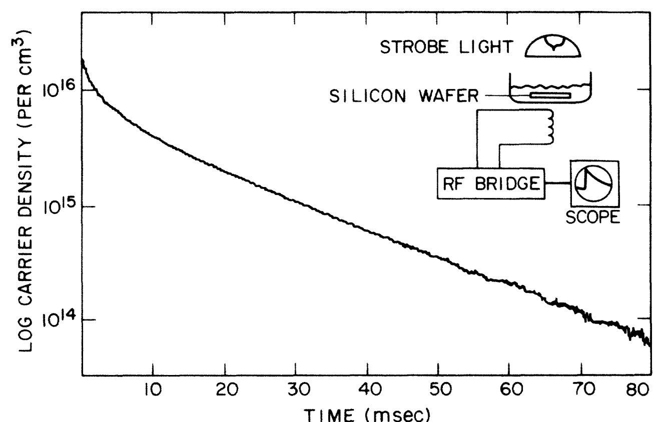

FIG. 1. Semilog plot of the carrier-density decay from a particularly long-lived 250-μm-thick Si⟨111⟩ sample immersed in HF acid.

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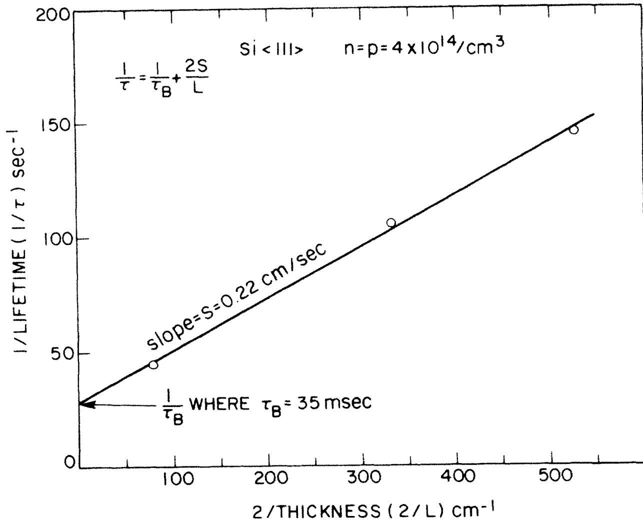

FIG. 2. When the decay rate at a given injection level is plotted against reciprocal thickness, the surface and bulk contributions can be distinguished as shown.

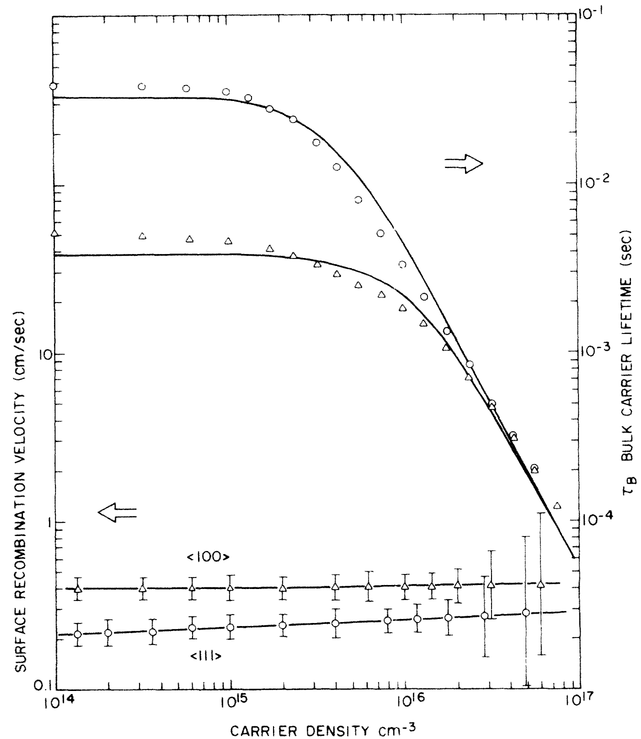

FIG. 3. Surface-recombination velocity and bulk lifetime vs carrier injection level for two different boules. The doping levels are negligible in this material. The lifetime curves (solid) are based on an Auger-recombination coefficient $=2\times10^{-30}$ cm^6/sec.

than the silicon which is used to make integrated circuits. Samples from this batch were then thinned to permit a reliable measurement of such a small surface effect.

A velocity of 0.25 cm/sec appears to be the lowest SRV ever reported. By comparison, surface recombination at the most carefully prepared[5] Si-SiO_2 interfaces is 5 to 10 times faster.[6] The SRV is sometimes modeled as $S=\sigma v_{\rm th}N_t$, where $v_{\rm th}\approx10^7$ cm/sec is the carrier thermal velocity, $\sigma\approx10^{-15}$ cm^2 is a typical recombination cross section, and N_t is the number of recombination centers per square centimeter. Under these assumptions the surface density of electronic defects is 2.5×10^7 cm^{-2} or less than 1 per 40 million surface atoms!

Shown in Fig. 3 is the dependence of SRV on the bulk-injection level for two samples of differing crystallographic orientation. It is interesting to note that on Si⟨100⟩ recombination is about 50% faster than on Si⟨111⟩. By contrast at the Si-SiO_2 interface it is the ⟨100⟩ surface which has the slowest recombination and the best electronic properties. The samples were very lightly doped at about 150 Ω-cm so that the doping density was negligible compared to the injected density at which the measurements in Fig. 3 were made, i.e., $n_b=p_b$. The injected-carrier density was calibrated by measuring the response of the rf bridge to wafers of known resistivity and correcting for the small variation of mobility with carrier density.[7]

There are two possible reasons for an extremely low SRV: (a) the presence of very few recombination centers on the surface and (b) the presence of a net surface charge which would bend the bands by an amount E, repelling one type of carrier from the surface and reducing the recombination velocity by $\exp(-E/kT)$. Such strong band bending, if it existed in this experiment, would depend sensitively on injected-carrier density which tends to flatten the bands by an amount $\Delta E=-kT\ln(n_b^{(2)}/n_b^{(1)})$ as the density changes from $n_b^{(1)}$ to $n_b^{(2)}$. Therefore, under strong band bending S would be linearly proportional to n_b increasing by a factor of 100 as n_b goes from 10^{14} cm^{-3} to 10^{16} cm^{-3} in Fig. 3. Since the actual measurement shows that S is virtually independent of bulk-carrier density over that range, it shows that strong band bending is absent. If the small residual increase actually observed within the error bars were entirely attributed to a net surface charge, it would place an upper limit[8] of 10^8 charges/cm^2 on such charge. This stringent limit is due to the particular sensitivity of the band bending to small amounts of charge when the bulk-carrier density is as low as 10^{14} cm^{-3}.

Similarly, we observed that the SRV remained low in n- or p-type material doped up to 10^{17} carriers/cm^3, which would have flattened the bands for the same reason as before. Therefore we conclude that the low SRV we observe is due to the presence of *very* few recombination centers at the surface. To the slight degree that band bending might be present, it produces a negligible effect on surface recombination.

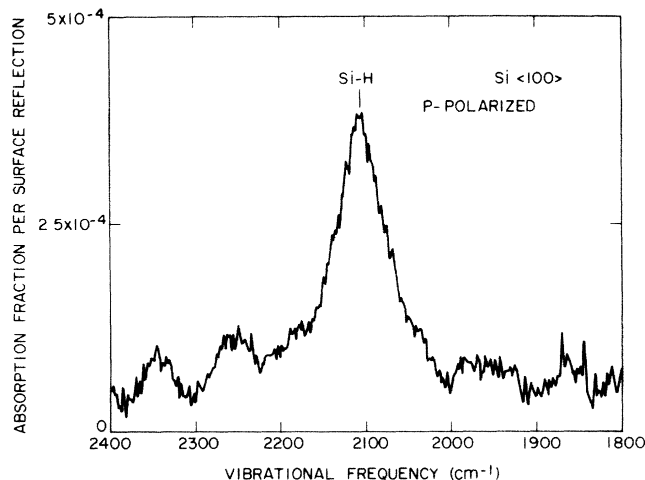

FIG. 4. Multiple-internal-reflection infrared-absorption difference spectrum showing about a monolayer of Si—H bonds on the surface.

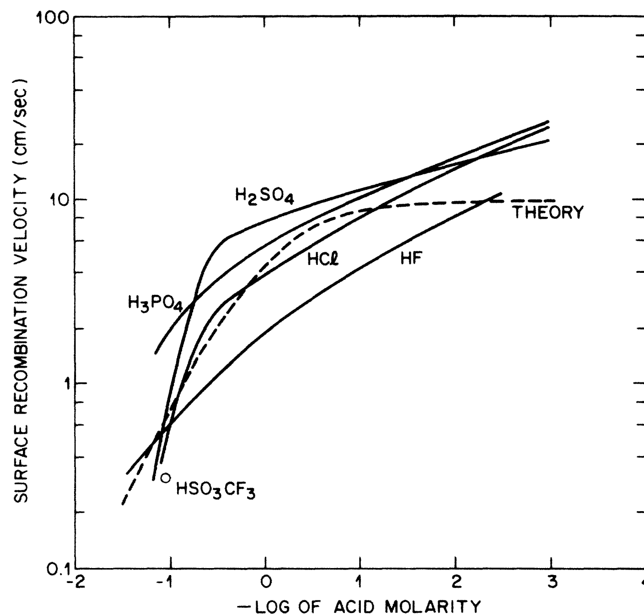

FIG. 5. Surface-recombination velocity for the properly prepared surface when immersed in various acids. For a 100% dissociating acid, −log(molarity) is the same as *p*H. The dashed theory line is an acid-base equilibrium model.

As a byproduct of the surface measurements we also obtain the bulk lifetime as a function of injection level as plotted in the top half of Fig. 3. This is the first measurement of Auger recombination in such a low-density range. In this range, it critically determines the ultimate efficiency[9] of silicon solar cells. The solid curve is a fit based on an Auger coefficient $=2\times10^{-30}$ cm^6/sec which is significantly more than the accepted value[10] extrapolated down from higher density. Furthermore the highest-density data points on Fig. 3 are also consistent with less Auger recombination. A reduction of Auger-recombination coefficient with increasing density was predicted by Vaitkus and Grivitskas.[11] These results suggest that Auger recombination will have a more serious effect on ultimate solar-cell efficiency than had previously been expected.[9]

We turn now to the chemical composition of the surface. Thermochemical grounds[12] suggest that the surface silicon atoms should be bonded to fluorine, since the Si—F bond is one of the strongest in chemistry. Indeed our earlier work[13] was interpreted with this assumption. However, x-ray photoemission shows only variable trace amounts of fluorine on the surface. Multiple-internal-reflection infrared spectroscopy indicates the pronounced presence of Si-H. Figure 4 is an infrared difference spectrum, i.e., the spectrum of a surface treated by HF acid minus that for DF acid. The integrated oscillator strength under the peak is equal to that attributed by Chabal[14] to full monolayer coverage by Si-H. At this coverage the difference between s and p polarization is much less pronounced than at lower coverages, and we did not observe a significant polarization dependence. Grunthaner and Grunthaner have studied[15] similarly prepared surfaces by x-ray photoemission and claim to have resolved the very tiny Si-H chemical shift in the Si $2p$ line.

We have found the Si-H covered surface to be quite robust. It is surprisingly slow to oxidize[16] under ambient conditions and can be handled in air and rinsed in water for brief periods. Thus we proceeded to measure the SRV as the initially prepared surface was then immersed in a series of acids of varying concentration. The results are plotted in Fig. 5. Some pertinent remarks are as follows: (1) Although HF acid is needed for the initial preparation of the surface, an outstanding SRV then occurs in a wide variety of concentrated acids. (2) The nonaqueous super-acid HSO_3CF_3 behaved similarly to the other acids. (3) The SRV seems to respond to acid molarity rather than *p*H since HF and H_3PO_4 are only weakly dissociating. (4) The effect of a change in concentration or composition of acid is *reversible,* at least for waiting periods < 15 min.

This last point suggests that an equilibrium model be invoked. In this model there is a finite surface concentration ($\approx10^9$ cm^{-2}) of strained, very weak bonds whose electronic levels can act as recombination centers. If we hypothesize that such centers resemble a Lewis base, then they can participate in an acid-base equilibrium with acid molecules in solution. To explain the electronic properties we assume that an acid-coordinated strained bond is shifted in energy so as to become inactive toward recombination. The acid-base equilibrium can be expressed as

$$x/(1-x)=K_{eq}/M, \qquad (2)$$

where K_{eq} is the equilibrium constant and M is the acid molar concentration. S is simply proportional to

x, the nonreacted fraction of surface defects which remain as recombination centers. This model is plotted as the dashed line in Fig. 5. Such a model suggests that the extraordinarily low SRV measured in concentrated acids may be due to the acid-base neutralization of a small finite density of surface defects, reducing their surface concentration even further.

We have also made some similar measurements on ultrahigh purity germanium crystals. There is no specific reason to believe that the chemistry should be the same, but we were able to produce SRV as low as 2 cm/sec on germanium surfaces. We would like to thank E. E. Haller for the loan of his germanium samples.

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