The clean Si(111)–2×1 surface: large nonequilibrium band curvature

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A large surface band curvature, ~10 eV, has been observed during interband (surface) optical absorption in *p*- and *n*-type silicon cleaved in ultrahigh vacuum.

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Whether of a volume or surface nature, the photo-emf of a semiconductor usually does not exceed its gap width. In some cases there is an anomalous photovoltaic effect, with the photo-emf reaching large values; the exact mechanism for this effect has not been finally resolved.[1] We have now observed an anomalously large surface photo-emf, at a level several times the gap width of silicon.

On clean Si(111)–2×1 surfaces of both *p*- and *n*-type silicon we studied the spectrum of the surface photo-emf, the temperature dependence of the work function, the temperature dependence of the photo-emf near the photon energy $h\nu = 0.45$ eV, and the kinetics of the photo-emf. The work function and the photo-emf were measured by the Kelvin method with a vibrating electrode and a constant illumination. A clean silicon surface (*p*-type silicon with a resistivity $\rho = 2000\ \Omega$·cm and *n*-type silicon with $\rho = 750\ \Omega$·cm) was obtained by cleavage along the (111) plane in a vacuum of 5×10^{-9} Pa.

In the spectrum of the photo-emf (Fig. 1) we can distinguish several characteristic intervals of the photon energy. For the *p*-type silicon (Fig. 1a), in the photon energy range $0.36\ \text{eV} < h\nu < 0.5$ eV with $h\nu_{max} = 0.45$ eV, we observed a positive photo-emf signal, while at photon energies $h\nu > 0.5$ eV we observe a negative photo-emf signal. The difference between the values of the photo-emf in these two regions reaches ~12 V. For the *n*-type silicon (Fig. 1b), we observe a negative signal with $h\nu_{max} = 0.45$ eV in the photon energy interval $0.36\ \text{eV} < h\nu < 0.72$ eV, while in the interval $h\nu > 0.72$ eV the photo-emf becomes positive. The difference between the values of the photo-emf for these two regions is ~10 V. When the surface is "oxidized" (exposed to O_2 for 10 Pa·s), the positive photo-emf signal for the *p*-type silicon and the negative photo-emf signal for the *n*-type silicon disappear, and the signal which remains amounts to several tenths of a volt.

The magnitude of the photo-emf signal (Δv_s) in the long-wavelength region ($h\nu \sim 0.45$ eV) depends on the direction of the light polarization with respect to the cleaved surface in the case of normal incidence: The ratio of the maximum signal to the minimum signal is ~2, and the angle between the polarization directions for these two signals is 90°. The value of Δv_s and the relaxation time of the signal (τ) both increase with decreasing temperature [$\Delta v_s \sim \exp(0.1/kT)$, $\tau \sim \exp(0.05/kT)$]. The time τ reaches values on the order of hundreds of seconds.

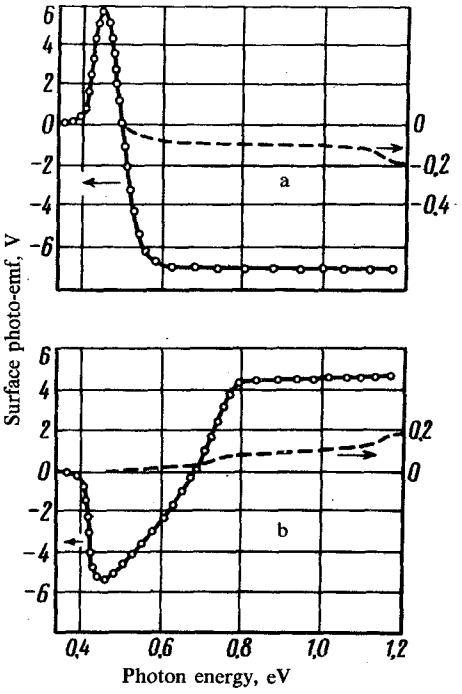

FIG. 1. Spectrum of the photo-emf for p-type silicon (a) and n-type silicon (b). $T = 90$ K, intensity of 10^{13} photons/(cm^2·s). Solid curves—clean surface; dashed curves—oxidized surface.

The work function of these surfaces of p- and n-type silicon remains essentially constant over the temperature range 300–120 K. Below 120 K, the work function begins to change exponentially [$\Delta\varphi \sim \mp \exp(0.16/kT)$]. For the p-type silicon, the work function decreases (becoming negative, in fact, while that for the n-type silicon increases. The magnitude of the change at $T = 90$ K is the same, within a few tenths of a volt, as the value of the photo-emf of the p-type silicon at $h\nu > 0.5$ eV and of the n-type silicon at $h\nu > 0.72$ eV (Fig. 1).

Although we do not yet have enough experimental information to offer an unambiguous description of these events, we can discuss some qualitative models which explain the results. On the clean cleaved Si(111)-2×1 surface there are two bands of surface states of "ruptured" bonds: a band of filled surface states and a band of unfilled surface states.[2–5] Transitions of electrons between these bands were observed in Refs. 3–5. The signal maximum corresponds to an energy of 0.45 eV and to a maximum of the combined state density of these two bands. The photon energy for the maximum of the photo-emf signal which we have observed and the polarization dependence of this maximum[5] imply that the signal at $h\nu \sim 0.45$ eV is due to optical transitions of electrons between the filled and unfilled surface states. The photo-emf is a change in the surface band curvature. For this emf to occur, there must be an exchange of charge carriers between the surface and the interior. In an effort to explain the slight band curvature, ~0.3 eV, for p-type silicon, Assmann and Mönch[5] suggest-

ed that nonequilibrium electrons from the filled surface states recombine with holes of the volume valence band. As the band curvature increases, however, this carrier-exchange mechanism ceases to make a substantial contribution to the photo-emf, since the concentration of majority charge carriers decreases significantly near the surface. It may be suggested that the exchange under these conditions results from a mechanism involving a diffusive motion of charge carriers through localized states, such as deep impurity levels in the space-charge region, dislocations, or one-dimensional cleavage steps.

An alternative explanation for the anomalously large photo-emf is based on the suggestion[1] that the effect is a manifestation of an anomalous photovoltaic effect. The asymmetric cell in which the elementary emf is generated acts to distort the surface band structure, namely the filled and unfilled surface states. This distortion is caused by the presence of cleavage steps, which are always present on a surface. The ("floating") potentials of the resulting emf on the surface tend to be distributed in such a manner that one potential is approximately equal to the substrate potential, while the

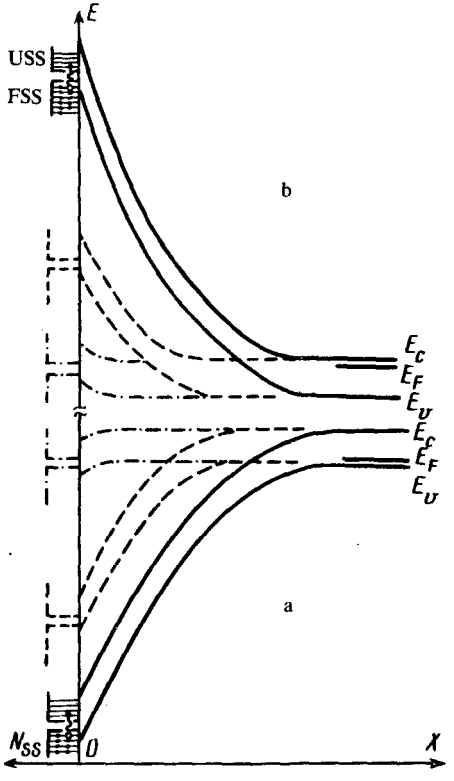

FIG. 2. Band scheme of the p-type (a) and n-type (b) silicon surfaces. USS—unfilled surface states; FSS—filled surface states; N_{ss}—density of surface states. Solid curves—Illumination at $h\nu = 0.45$ eV; dashed curves—illumination of $h\nu = 0.9$ eV; dot-dashed curves—no illumination. Here E_c, E_v, and E_F are respectively the conduction band, the valence band, and the Fermi level.

other produces a depletion layer in the substrate. In measuring the photo-emf we are measuring an average potential.

Before the illumination, the space-charge region for the p- and n-type silicon is thus a depleted layer, while after the illumination ($h\nu \sim 0.45$ eV) the original band curvature increases (Fig. 2). The formation of an inversion layer is hindered by the low rate at which minority charge carriers are generated (because of the low temperature) and also by the recombination of these carriers with nonequilibrium charge carriers of one of the bands at the surface: filled surface states in the case of the p-type silicon and unfilled surface states in the case of the n-type. The reason for the change in the sign of the photo-emf in the short-wave part of the photon energy range is the onset of an additional mechanism. This additional mechanism involves the transition of electrons from the volume valence band to deep impurity levels in the space-charge region or in the unfilled surface states (for the p-type silicon) or from deep impurity levels or surface states into the volume conduction band (for the n-type silicon).

These results show that the change in the work function with decreasing temperature is also associated with the presence of a nonequilibrium radiation, since the reference electrode and the sample are at different temperatures.

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[1]J. I. Pankove, Optical Processes in Semiconductors, Prentice-Hall, Englewood Cliffs, NJ (Russ. transl. Mir, Moscow, 1973, p. 346).
[2]F. G. Allen and G. W. Gobeli, Phys. Rev. **127**, 150 (1962).
[3]G. Chiarotti, S. Nannarone, R. Pastore, and P. Chiaradia, Phys. Rev. **B4**, 3398 (1971).
[4]H. Froitzheim, H. Ibach, and D. L. Mills, Phys. Rev. **B11**, 3917 (1975).
[5]J. Assmann and W. Mönch, Surf. Sci. **99**, 34 (1980).

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