# Observation of Multiple Peaks in Field-Emission Energy Distributions from Silicon

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Field-emission energy distributions are presented for $n$-type Si (0.001 Ω cm), with both field-desorbed and flash-recrystallized surfaces, indicating that emission occurs primarily from surface states ~0.4 eV below the Fermi level, $E_F$, and lower. At reduced temperature and high field, emission begins to appear at higher energy up to $E_F$. Further, for smooth, recrystallized surfaces, multiple peaks are observed in the energy distributions, of 0.1- to 0.2-eV separation.

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Field emission from metal surfaces is well understood.[1] This is not the case for semiconductors, where experimental energy distributions from different workers show little agreement either to each other or to established theory.[2-6]

The theoretical form of energy distributions for semiconductors was generalized by Stratton[7] from the original work by Young.[8] This theory takes account of the valence and conduction bands only, excluding surface-state emission. For a multivalley semiconductor such as Si, Stratton's formalism predicts a substantially reduced tunneling probability for conduction electrons in directions other than the ⟨100⟩. Thus, the valence band may actually dominate the emission even for degenerately $n$-type samples. However, for direct-gap semiconductors, such as GaAs, conduction-band tunneling is isotropically preferred.

Previous experimental energy distributions from semiconductors do not agree with this theory. The distribution from 0.0005-Ω-cm $n$-GaAs,[3] for example, shows only one peak, starting almost 1 eV below the collector Fermi level with a full width at half maximum of 0.5 eV, substantially wider than predicted by the theory for conduction-band emission. This was concluded by the authors to be evidence of valence-band or surface-state emission. For Ge, a similar situation was obtained by Shepherd and Peria,[4] who found that emission predominated from a narrow band of surface states, attached to a wide tail ascribed to valence-band emission. The Ge surface in this case was presumed to be degenerately $n$ type.

For Si, two groups have reported experimental distributions. The first[5] reported two symmetric peaks, whose maxima were separated by the band-gap energy. These peaks were attributed to the valence and conduction bands. The peaks, however, tailed into the gap region, where emission is forbidden in the Stratton formalism. A second group[6] reported seeing one or two peaks. The single peak widened with increasing field, and the double peaks were very wide, with separations of 1 to 2.2 eV. The lower of the double peaks was again ascribed to valence-band emission.

We report the following observations on 0.001-Ω-cm Sb-doped (110)-oriented Si, using a van Oostrom-type analyzer[9] with an Au-coated spherical collector. First, the 300-K field-desorbed energy distribution, curve $A$ in Fig. 1, comprised a single peak which appears below the measured Fermi level by ~0.4 eV. Increasing the field shifts this distribution down in energy

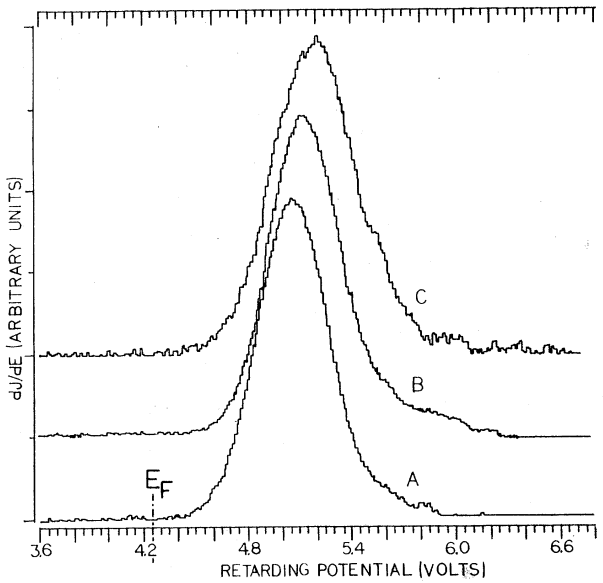


FIG. 1. Energy distributions for Si at 300 K, field-desorbed surface. Curve $A$, 4000 V (~0.30 V/Å); curve $B$, 4480 V (~0.34 V/Å); curve $C$, 4750 V (~0.36 V/Å).

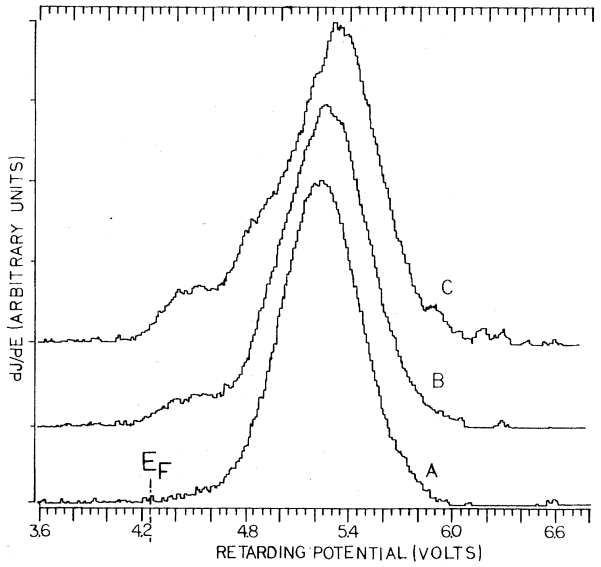


FIG. 2. Si at 78 K, field-desorbed surface. Curve $A$, 4700 V (~0.36 V/Å); curve $B$, 4950 V (~0.38 V/Å); curve $C$, 5150 V (~0.39 V/Å).

and increases the width, as in curves $B$ and $C$.

Cooling the same desorbed surface to 78 K results in a similar distribution at low fields, shown in curve $A$ of Fig. 2. Increasing the field again shifts the distribution down in energy, as shown in curve $B$. But emission now appears at $E_F$ and below. On increasing field, this higher-energy emission increases in magnitude relative to the lower peak, which continues to shift down in energy and broaden, curve $C$.

By increasing the field-emission current beyond a critical density, the tip end melts abruptly. The radius increases and the recrystallized surface is smoother than that obtained by prolonged annealling. The observation of these smooth surfaces indicated that the structural details seen previously for Si are indeed due to faceting.[10] Further, the lack of detail of the recrystallized surface appears qualitatively to indicate a uniform work function for the emitter surface.

Surprisingly, we have observed a new structure in the energy distributions for such smooth surfaces. These distributions contain sharp peaks, whose half-widths vary from 0.11 eV to approximately 0.2 eV. Shown in Fig. 3 are three successive runs, taken 30 min apart, just after the smooth surface was obtained in $4\times10^{-11}$ Torr. The emission direction for this set was [421], near the dark (311) plane. For the other surface emission was directed along the [110] axis, and

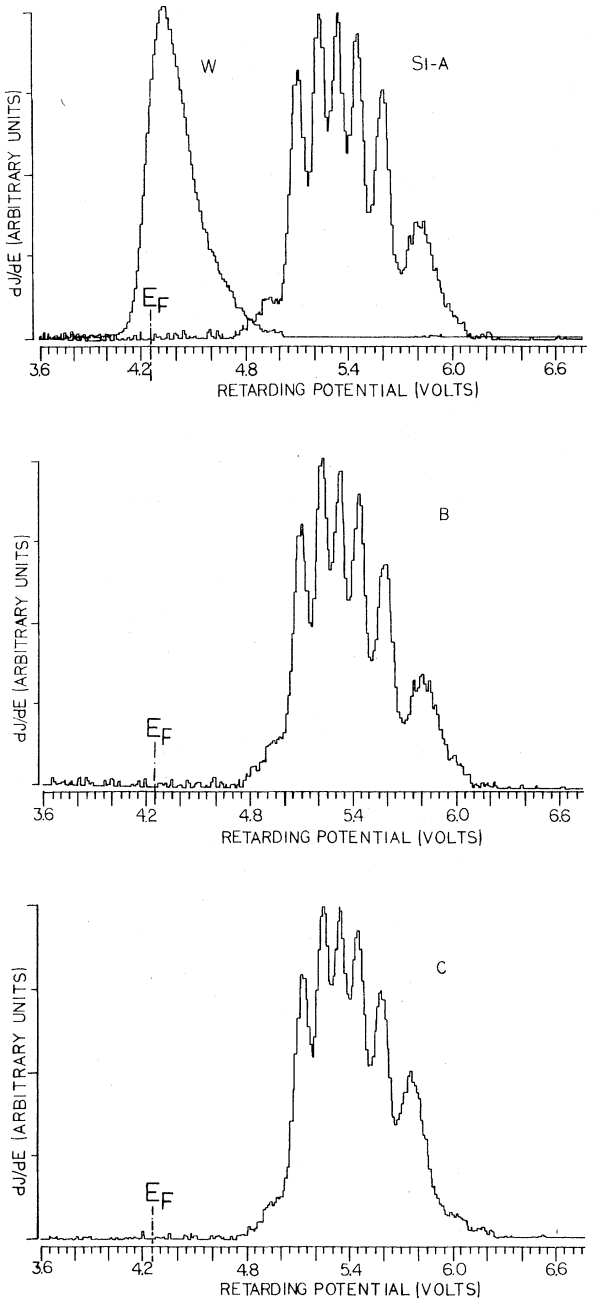


FIG. 3. Flash-recrystallized, smooth Si surface. (a) 30 min after recrystallization, 6515 V; (b) 30 min later, 6515 V; (c) 30 min later, 6550 V. Distribution from a W surface at 78 K is also shown for comparison.

showed peaks which appeared better resolved but were less well reproduced.

The number of peaks observed increased with increasing field. However, the peak separation changed only slightly with increasing field, tend-

ing toward closer spacing of high-energy levels. The lower-energy peaks are consistently more separated in energy than the high-energy peaks, implying that these may be emission from quantized states of a potential well.

In the absence of surface states, the conduction band will be pulled below $E_F$ by the applied field, creating a potential well. Yatsenko[11] has calculated the spacing of these levels; they are spaced from 0.1 to 0.2 eV. The coincidence between the calculated spacing and our observed spacing indicates this possibility. However, this explanation is inconsistent with the results of the data presented in Figs. 1 and 2, which show that at 300 K, emission comes from states 0.4 eV below $E_F$ and lower.

The photoemission work of Wagner and Spicer[12] on Si of the same doping ($N_D = 10^{19}$–$10^{20}$) was interpreted to be due to a band of surface acceptor states, beginning at 0.57 eV below the conduction-band edge. The charge on these acceptor states, under thermal equilibrium, with no applied field, resulted in an internal field, opposite in direction to a field-emission field, of about 0.65 V/Å,[13] comparable to the field-emission field. Thus the effect of the applied emission field will be to flatten the bands at the surface. This will lower the surface-state band, yet may still prevent conduction-band electrons from escaping because of the residual barrier, which we estimate to be 0.23 eV at a field of 0.4 V/Å. The amount of lowering of the surface-state band will be about 0.4 eV. This is approximately the position of the distribution edge below $E_F$ for the Si surfaces we observed at 300 K.

At lower temperature, the surface-state density remains constant. However, the carrier concentration in the Si drops. During the emission process, the surface states will empty, and must be refilled by free carriers from the bands. Obviously if the carrier concentration is reduced, either by reduced doping, compensation, or reduced temperature, the surface states may become depleted. This will allow the field to penetrate into the surface, and will both lower the surface-state band and pull the conduction band into accumulation. As seen in Fig. 2 and also observed by Kleint and Kusch,[6] and perhaps Kisker, Mahan, and Reihl,[14] this yields two peaks of varying separation, with the higher peak occurring at the Fermi level.

In conclusion, it appears that field emission from semiconductors occurs primarily from surface states below $E_F$ in thermodynamic equilibrium. However, at reduced temperature or equivalently reduced doping, the rate of repopulation of the surface states is reduced. Field penetration will then shift the depopulated surface-state band down in energy and allow conduction electrons to escape at higher energy. In addition, depending upon surface conditions, sharp peaks are observed in the energy distributions from these surface states. Though the separation of these peaks is the same as predicted by conduction-band accumulation at fields of $0.2/\epsilon$ to $0.4/\epsilon$ V/Å ($\epsilon$ is the dielectric constant), we ascribe these to surface states for the above reasons. Further, the width of the distributions shows little agreement with predictions of Stratton's generalized theory of emission from bulk states, indicating that the nature of the initial states differs from the known behavior of ascribed bulk-state emission for metallic emitters.

To our knowledge, no theory for surface-state properties predicts the existence of the sharp structure we observe. The Tamm calculation leads to a single state per band gap, while the Schockley model provides a rationale for a band of surface states, depending upon spatial density of the atomic potentials. Because of the slight dependence on field strength that we observe, these peaks may be the result of an interaction of a smooth surface potential with the image potential which changes with field.

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# Experimental Evidence for One Highly Dispersive Dangling-Bond Band on Si(111) 2 × 1

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Angle-resolved photoemission data along the $\bar{\Gamma}$-$\bar{J}$ symmetry line in the surface Brillouin zone of the Si(111) 2×1 surface show that there exists only one dangling-bond band. This fact removes the experimental basis for the introduction of electron correlation effects for the Si(111) 2×1 surface. The dangling-bond band shows a large positive energy dispersion, which favors the recently suggested $\pi$-bonded chain model instead of the widely considered buckling model.

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In this Letter we present new angle-resolved photoemission results which provide evidence for the existence of *one* dangling-bond surface-state band on the Si(111) 2×1 surface. This dangling-bond band shows a large positive initial-state energy dispersion along the $\bar{\Gamma}$-$\bar{J}$ symmetry line in the 2×1 surface Brillouin zone (SBZ). This result is in agreement with measurements, in which the dispersion relations along the $\bar{\Gamma}$-$\bar{J}$ and $\bar{\Gamma}$-$\bar{K}$ symmetry lines in the 2×1 SBZ for both the dangling-bond and the back-bond surface-state bands were obtained.[1]

The initial-state energy dispersion relation for the dangling-bond band presented here is in disagreement with a recent photoemission study,[2] where the existence of *two* dangling-bond bands along the $\bar{\Gamma}$-$\bar{J}$ symmetry line was suggested. Our results are also in qualitative disagreement with calculated dispersion relations obtained from the buckling model,[3-6] which has so far been the most widely accepted model for the 2×1 reconstruction of the Si(111) surface.

Experimentally determined dangling-bond bands along the $\bar{\Gamma}$-$\bar{J}'$ symmetry line[7,8] have failed in providing conclusive comparison with the calculations, since the buckling model gives bands with small dispersion, and the experiments have not been consistent concerning the magnitude of the dispersion. Experiments which present results along the $\bar{\Gamma}$-$\bar{J}$ or $\bar{\Gamma}$-$\bar{K}$ symmetry lines[6,9] have indicated a dangling-bond band with a large positive dispersion from $\bar{\Gamma}$ to $\bar{J}$ and $\bar{K}$, respectively. A new "$\pi$-bonded chain model" proposed by Pandey[10] gives a single dangling-bond band with a positive dispersion from $\bar{\Gamma}$ to $\bar{J}$. The dispersion relation obtained from this chain model is similar to the experimental dispersion presented here, and is also consistent with the existence of only one experimental dangling-bond band.

Angle-resolved photoemission spectra were measured in a UHV chamber at a pressure of $5\times10^{-11}$ Torr. The photoelectrons were excited with use of monochromatized 10.2-eV radiation from a hydrogen discharge. The electrons emitted were energy analyzed by a 180° spherical deflection analyzer rotatable in the plane of light incidence. Monochromator slits and analyzer voltages were set to give a combined energy resolution of $\leq 0.15$ eV in the recorded spectra.

The samples were made from a Si(111) single crystal of $p$ type ($\rho \sim 43\ \Omega$ cm), cut into bars with a square cross section of 5×5 mm$^2$. The Si(111) bars were cleaved in UHV and on each bar three different cleavages could be made.

Angle-resolved spectra were obtained from both single and multidomain cleavages.[11] In contrast to some earlier reports,[8] we have found a very high degree of reproducibility of the electronic structure for different cleavages. For surfaces with more than one domain, the spectra are con-