ments are consistent with previous studies made on the nonanomalous part of the resistivities for the Pd-Si[14] and the Ni-Pd-P alloys.[15] It was concluded that the resistivity was due to the amorphous nature for the Pd-Si case and mainly to spin fluctuations for the Ni-Pd-P case. Other amorphous alloys which behave similarly to the Ni-Pd-P are the Ni-Pt-P alloys. We expect various anomalies of the present kind in these alloys.[16]

Although the concentration of heavy atoms such as Ni and Pd is large in the amorphous alloys studied, resistivity behavior in the form of Eq. (1) has not been found. This does not necessarily mean that the spin-orbit interactions are negligible in these alloys. We have to wait for a proper theory of the effect possibly based on the treatment of Everts and Keller.

It is a pleasure to thank Professor Pol Duwez for his interest in the present work.

*Work supported by the U. S. Atomic Energy Commission.

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Photoemission Densities of Intrinsic Surface States for Si, Ge, and GaAs†

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(Received 28 March 1972)

Photoemission-energy-distribution measurements of intrinsic surface states for Si, Ge, and GaAs have been made using synchrotron radiation in the 7–25-eV range. Occupied intrinsic surface states with Gaussian-shaped optical densities of states about 0.8 to 1.0 eV wide, centered at 0.75, 0.7, and 1.05 eV below the Fermi level, are observed for Si, Ge, and GaAs, respectively. These bands are centered at about 0.45, 0.75, and 0.5 eV below the valence-band edge E_v, respectively, rather than at or above E_v as has been generally concluded.

Intrinsic surface states are well known to exist in or near the energy gap of semiconductors such as Si, Ge, and GaAs and have been the subject of many recent studies, including measurements of photoelectric threshold, work function, and band bending,[1-4] electron-spin resonance (EPR),[5] optical absorption,[6] conductivity,[4] and, recently, photoemission energy distributions.[7] A quantity of general interest which most experiments relate to in one way or another is the density of surface states, whose shape has not been known. Assuming that bulk- and surface-state photoemission can be separated (which we show can be done straightforwardly at high photon energies $h\nu$), photoemission-energy-distribution measurements afford a way of determining rather directly the overall shape of the occupied density of surface states.

We report such photoemission measurements for Si, Ge, and GaAs, made in the range $7 \lesssim h\nu \lesssim 30$ eV using intense synchrotron radiation. For lightly doped n-type ($\sim 10^{15}$ cm^{-3}) Si and Ge and

for lightly doped n-type GaAs, we observe bands of occupied intrinsic surface states with Gaussian-shaped optical densities of states about 0.8–1.0 eV wide centered at 0.75, 0.7, and 1.05 eV below E_F, respectively; i.e., considering band bending, centered at about 0.45, 0.75, and 0.5 eV *below* the valence band edges E_v, respectively. Our results differ from those previously reported in that it has been generally concluded (at least for Si)[1-6] that the occupied surface states are in a narrower band which primarily lies between E_F and the valence-band edge. Recent photoemission-energy-distribution measurements for degenerate n-type Si by Wagner and Spicer[7] are in overall agreement with our Si measurements.

Photoemission energy distributions were measured in the range $7 \leq h\nu \leq 30$ eV using a two-stage cylindrical-mirror electron analyzer and synchrotron radiation from the 240-MeV storage ring at the University of Wisconsin Physical Sciences Laboratory.[8] For data in Figs. 1 and 2, the electron analyzer was used with a ~0.12-eV energy resolution, and the 1-m normal-incidence monochromator resolution was ~0.09 eV at $h\nu \leq 12$ eV, ~0.13 eV at $h\nu = 20$ eV, and ~0.35 eV at $h\nu = 26$ eV. Likewise, signal-to-noise ratios decreased from ~300:1 for $h\nu \leq 12$ eV to ~100:1 for $h\nu = 26$ eV. Fermi level positions were determined by evaporating metal films onto the semiconductor surface *in situ*; typical results for Cu deposited on Ge are shown in Fig. 2 (Cu edge). This Cu edge also gives a measure of the resolution (the Fermi distribution gives it an intrinsic width of ~0.12 eV).

We studied single crystals of 5-Ω-cm (~10^{15} cm^{-3}) n-type Si (111), 4-Ω-cm (4×10^{14} cm^{-3}) n-type Ge (111), and lightly doped n-type GaAs (110) of 4 and 6 mm length. Lightly doped samples were used to avoid complications and smear-

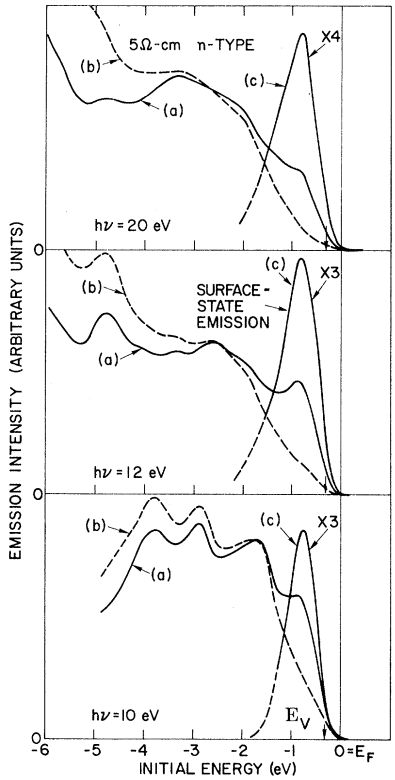

FIG. 1. Energy distributions for Si. Curves *a* were measured within ~30 min after cleaving in $\sim 3\times10^{-10}$ Torr and show bulk plus surface-state emission. Curves *b* were measured about 7 h later, by which time the surface-state emission has largely vanished. Curves *c* are the differences of *a* and *b* and depict the optical density of intrinsic surface states.

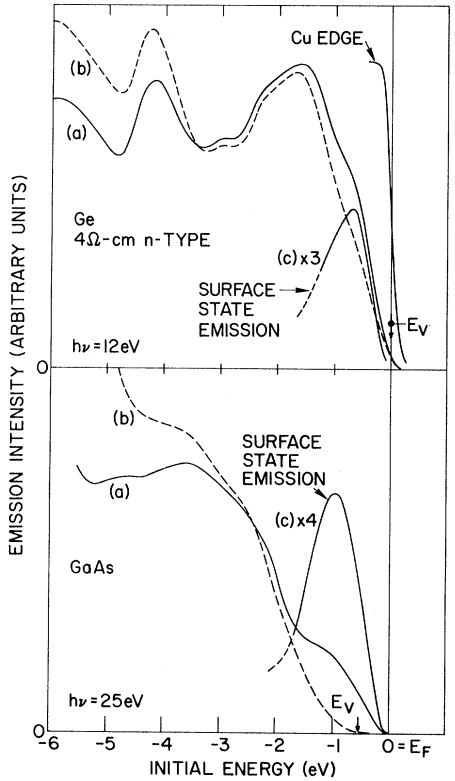

FIG. 2. Energy distributions for Ge and GaAs. For Ge, curve *a* was measured about 1 h after cleaving ($p \sim 1\times10^{-9}$ Torr), and curve *b* was measured after exposure to $\sim 2\times10^{-6}$ Torr min of air. For lightly doped n-type GaAs, curve *a* was measured about 15 min after cleaving and curve *b* was measured about 1 day later ($p \sim 3\times10^{-10}$ Torr). The difference curves *c* denote the optical densities of intrinsic surface states. For GaAs, this density of states is broadened by about ~0.35 eV by the photon band pass.

ing effects due to short band-bending depths. For both Si and Ge crystals with our doping levels, the bulk Fermi levels lie ~0.25 eV below the conduction-band minima E_c, and we obtain upward surface-state band bendings of ~0.5 and 0.4 eV, respectively, using $E_F - E_v$ from Refs. 1 and 3. For n-type (110) GaAs, surface states bend the bands upwards, with E_F reported at about 0.5–0.6 eV above the valence-band maxima for 10^{16}–10^{17}-cm^{-3} doped samples.[9] All curves a and c in Figs. 1 and 2 are referred to E_F, which has been determined to ±0.05 eV, and the energy positions of valence-band edges E_v given by the above-mentioned band-bending measurements[1,3,9] are shown.

Photoemission measurements of intrinsic surface states for Si are summarized in Fig. 1, where energy distributions are shown for photon energies of 10.0, 12.0, and 20.0 eV. Curves denoted by a in Fig. 1 show the sum of bulk- and surface-state emission for an n-type 5-Ω-cm single crystal of area 2×2 mm^2 and (111) orientation. Si crystals were cleaved (with some faceting) in vacuum (mid-10^{-10}-Torr range) and then measured within ~30 min. The intrinsic surface states were then largely removed by gas exposure (either by simply waiting ~6–7 h at p ~ mid-10^{-10} Torr or by air exposure (~2×10^{-6} Torr min), which is well known to remove intrinsic surface states[4-6] and create extrinsic surface states. Curves b in Fig. 1 show the measured energy distributions after removal of the intrinsic surface states. We observed a decrease in band bending of ~0.09±0.02 eV, and curves b in Fig. 1 are shifted by this amount so as to subtract the bulk emission from curves a. The differences between curves a and b are then a direct measure of the optical density of intrinsic surface states and are shown in Fig. 1 (curves c, with amplifications as shown). Extrinsic surface states (probably Si-O) are formed after gas exposure and are observed to form a broad band centered near 7 eV below E_F. The upper edge of this band is seen in Fig. 1 as extra emission below −5 eV for $h\nu = 12$ and 20 eV.

Our optical density of surface states in Fig. 1 shows a band about 0.8 eV wide (full width at half-maximum) centered at 0.75 eV below E_F (i.e., at ~0.45 eV below the top of the valence-band edge, which lies at ~0.32±0.08 eV below E_F[1,2] because of band bending), with a tail of surface-state density which extends up to E_F. Evidence that our optical density of surface states (curves c in Fig. 1) is a measure of the density of intrinsic surface states is at least threefold: (a) our observed sensitivity to gas exposure, which is in agreement with many other studies[4-6]; (b) the observation (shown in Fig. 1) that the energy distribution of surface-state emission is essentially independent of photon energy (i.e., all curves c have the same shape) over the wide range $10 \leq h\nu \leq 20$ eV, while that of bulk emission changes markedly in peak positions and amplitudes; and (c) our observation that surface-state emission increases in intensity relative to bulk emission as $h\nu$ increases from 7 to 12 eV. This is the expected trend since the bulk hot-electron escape depth is decreasing with increasing energy in this range. Observation (b) indicates that surface-state and bulk emissions are due to nondirect (i.e., crystal momentum $\vec{k}$ not conserved) and to direct optical excitations, respectively. This behavior is expected since the localization of the surface states should largely destroy the effect of $\vec{k}$ conservation for surface-state excitations. Concerning observation (c), we have measured the intensity of surface-state emission relative to bulk emission within ~3 eV of E_F for $h\nu = 8.5$, 10, and 12 eV. We can make a very rough estimate of the energy-dependent bulk escape depth if we make the following assumptions: (1) roughly one surface state per surface atom,[4] (2) equal transition probabilities for bulk- (about 1.3 states per atom within 3 eV of E_v) and surface-state optical excitations, and (3) an energy-dependent free-electron surface escape probability. In this way we obtain a hot-electron scattering length of about 25 atom layers (~40 Å) at $h\nu = 8.5$ eV, 11 atom layers (~17 Å) at $h\nu = 10$ eV, and 4 atom layers (~6 Å) at $h\nu = 12$ eV. Within the bounds of our crude assumptions, these scattering lengths agree with the calculation of Kane,[10] who obtained a scattering length for Si of ~30 Å at $h\nu = 8.5$ eV which is decreasing with increasing energy. Both the calculation[10] and our experiment are probably uncertain by a factor of 2.

Photoemission-energy-distribution measurements of intrinsic surface states for Ge and GaAs are shown in Fig. 2. As with Si, curves a, b, and c refer to freshly cleaved surfaces, gas exposed surfaces, and the resulting optical density of surface states, respectively. For Ge, curve b corresponds to ~2×10^{-6} Torr min of air exposure, and a small ~0.03-eV decrease in band bending accompanied the disappearance of surface states near E_F. For GaAs, curve b corresponds to a 1-day exposure to residual gas in the vacuum system (p ~ 2×10^{-10} Torr), and a 0.15-eV decrease in band bending accompanied the disap-

pearance of surface states near E_F. Curves *b* are shifted by these changes in band bending so as to subtract bulk emission.[11] Ge and GaAs show bands of intrinsic surface states about 0.9 ± 0.2 eV wide centered at about 0.7 and 1.05 eV below E_F, respectively, i.e., at about 0.75 and 0.5 eV below the valence-band maxima E_v. For Ge, a tail of surface states extends essentially up to E_F, while for GaAs there appears to be a gap (~ 0.3 ± 0.1 eV) just below E_F in which the optical density of surface states is very small.[12] For GaAs, the amplitude of surface-state emission appeared to decrease with time faster than might be expected for gas exposure with $p \sim 3 \times 10^{-10}$ Torr. The surface-state emission intensity shown in Fig. 2 was measured about 15 min after cleaving and decreased by about a factor of 4 within the next 45 min.

For Si, the shape of our optical density of states of intrinsic surface states near E_F is similar to the hyperbolic-cosine-like curve (one of several models) which Allen and Gobeli[1] concluded was consistent with their studies of work function and photothreshold versus doping, and which has been used by others.[3,13] If we normalize our optical density of states to contain about one occupied surface-state electron per surface atom, out resulting number of surface states within ~ 0.1 eV of E_F is roughly $\frac{1}{4}$ that previously reported.[1,2] This might be due to our crude assumptions such as constant matrix elements or might simply be due to inaccuracies in the shape of our ODS near E_F, since the charged surface states involved in reported work-function measurements[1,2] are roughly $\lesssim 1\%$ of the total number of surface states.

The able assistance of members of the storage-ring group at the Physical Sciences Laboratory is gratefully acknowledged.

†Work supported in part by the U. S. Air Force Office of Scientific Research under Contracts No. F44620-70-0089 and No. F44620-70-C-0029.

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[11]The amplitudes of curves *b* in Figs. 1 and 2 were scaled so as to be about equal to curves *a* at ~ 2–3 eV below E_F; this scaling assumes that essentially all of the emission from ~ 2–3 eV below E_F is bulk emission. Slight changes in the relative amplitude of curves *b* will not significantly change our surface-state emission curves *c*.

[12]This 0.3-eV gap was determined from data for $h\nu = 20$ eV, for which the photon band-pass broadening $\Delta h\nu$ was less. The gap shown in Fig. 2 is narrowed by about $\frac{1}{2}\Delta h\nu$ or ~ 0.2 eV, and also the width of the optical density of states is broadened by ~ 0.3 to 0.4 eV.

[13]Ref. 4, p. 120.

Observation of a Band of Silicon Surface States Containing One Electron Per Surface Atom*

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(Received 31 March 1972)

We have studied the energy distribution of electrons photoemitted from surface states on the cleaved (111) face of a 0.001-Ω-cm *n*-type Si crystal. We find a 1.8-eV-wide surface band with a peak at 1.1 eV and a shoulder at 0.5 eV below the Fermi energy containing about 8×10^{14} electrons/cm^2, i.e., approximately one electron per surface atom. The strong peak lies below the valence-band maximum at the surface. The surface nature of this structure is confirmed by its disappearance when exposed to vacuum contamination at 10^{-10} Torr or to oxygen.

Information about surface states on silicon can be inferred from an analysis of work function and photoelectric threshold measurements as shown by the pioneering work of Allen and Gobeli,[1] whose techniques have been refined by Fischer.[2] Eden[3] has identified photoemission from the sili-