

bosons, we obtain

$$\begin{aligned}
 A &= p^2 - \epsilon - \frac{1}{2}T \int_{-\infty}^{\infty} G_1 \ln(1 + e^{-\epsilon/T}) dk - \frac{1}{2}T \int_{-\infty}^{\infty} G_1 \ln(1 + e^{-\psi/T}) dk - \frac{1}{2}T \int_{-\infty}^{\infty} G_0 \ln[1 + \exp(\varphi_1/T)] dk, \\
 C &= -\psi + A - p^2 + \epsilon, \\
 \varphi_1 &= \frac{1}{2}T \int_{-\infty}^{\infty} G_0 \{ \ln[1 + \exp(\varphi_2/T)] - \ln(1 + e^{-\epsilon/T}) - \ln(1 + e^{-\psi/T}) \} dk, \\
 \varphi_n &= \frac{1}{2}T \int_{-\infty}^{\infty} G_0 \{ \ln[1 + \exp(\varphi_{n+1}/T)] + \ln[1 + \exp(\varphi_{n-1}/T)] \} dk, \quad n \geq 2, \\
 B &= \lim_{n \rightarrow \infty} \frac{1}{2}T \int_{-\infty}^{\infty} G_0 \{ \ln[1 + \exp(\varphi_{n+1}/T)] - \ln[1 + \exp(\varphi_n/T)] \} dk,
 \end{aligned} \tag{23}$$

with

$$\rho = -(2\pi)^{-1} (1 + e^{\epsilon/T})^{-1} \partial \epsilon / \partial A, \quad \tau = -(2\pi)^{-1} (1 + e^{\psi/T})^{-1} \partial \psi / \partial A, \quad \sigma_{n,n} = -(2\pi)^{-1} [1 + \exp(\varphi_n/T)]^{-1} \partial \varphi_n / \partial A;$$

and

$$E/L = \int_{-\infty}^{\infty} p^2 \rho(p) dp, \quad N/L = (M_1 + M_2 + M_b)/L = \int_{-\infty}^{\infty} \rho dp, \tag{24}$$

$$M_b/L = \int_{-\infty}^{\infty} \tau dp, \quad (M_1 - M_2)/L = \lim_{n \rightarrow \infty} \int_{-\infty}^{\infty} \sigma_{n,n} dp,$$

$$\frac{F}{L} = A \frac{N}{L} + C \frac{M_b}{L} - \frac{T}{2\pi} \int_{-\infty}^{\infty} \ln(1 + e^{-\epsilon/T}) dk - B \left(\frac{M_1 - M_2}{L} \right). \tag{25}$$

All the details will be published elsewhere.

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Strain-Induced Inhomogeneity of the Surface Potential on Freshly Cleaved Semiconductor Surfaces*

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Photoelectric emission and work-function measurements on GaSb have shown that the surface potential, and therefore the band bending and work function, of freshly cleaved surfaces present variations of up to 0.5 eV over macroscopic distances along the surface. These properties vary over a period of several days at room temperature in the sense that band bending increases and inhomogeneities disappear, suggesting annealing of cleavage-induced strains or defects. The electron affinity and ionization energy of freshly cleaved surfaces are well defined: They do not present spatial or temporal variation. Related observations were made on InP and GaAs.

Cleavage in ultrahigh vacuum¹ is a classical method for preparing clean and well-defined semiconductor surfaces. It has the advantage of being simple and of producing unquestionably

clean surfaces with unchanged doping and stoichiometry of the material in their vicinity. Such surfaces also produce excellent low-energy electron-diffraction patterns which, however, often

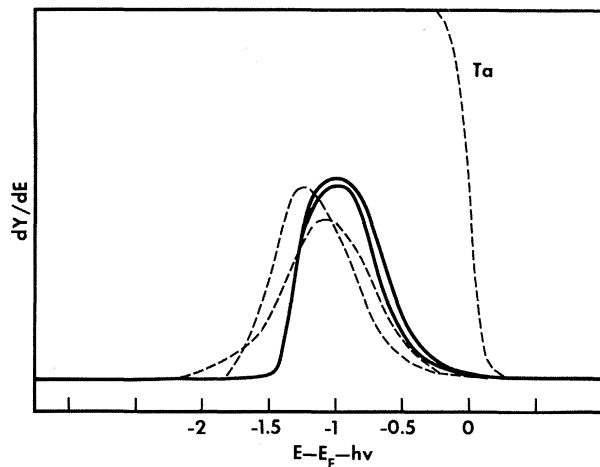


FIG. 1. Energy distributions of photoelectrons from GaSb that was freshly cleaved (dashed curves) and aged at room temperature (solid curves) for several days.

change upon annealing.²

Frankl³ has warned that cleavage introduces plastic deformations which might have an effect on electronic properties, and that therefore cleaved surfaces might not be sufficiently homogeneous and reproducible to be considered a well-defined state of matter. We present experimental evidence supporting this view.

Figure 1 shows energy distributions of photoemitted electrons from two (110) surfaces of GaSb obtained by repeated cleavage of the same *n*-type crystal ($N_D - N_A = 4 \times 10^{17} \text{ cm}^{-3}$). Measurements were performed within 2 h after cleavage (dashed curves) and again after the surfaces had remained at room temperature in vacuum ($p < 10^{-10}$ Torr) for more than 2 days (solid curves). The position of the Fermi level with respect to the energy of the electrons prior to excitation, i.e., the valence band, is determined with the help of the energy distribution of photoelectrons from a metal.⁴

We observed in Fig. 1 that the freshly cleaved surfaces produce energy distributions with ill-defined low-energy ends. The latter are also different for the two cleavages. This feature indicates that the work function of the material is not uniform over the size of the illuminated surface ($1 \times 5 \text{ mm}$). This variation of the work function was also observed by measuring the contact potential with a Kelvin probe on different sites on the surface. The readings differ by as much as 0.5 eV, which is consistent with Fig. 1.

The distributions obtained after 2 days display sharp low-energy ends which are the same for both cleavages: The work function has become

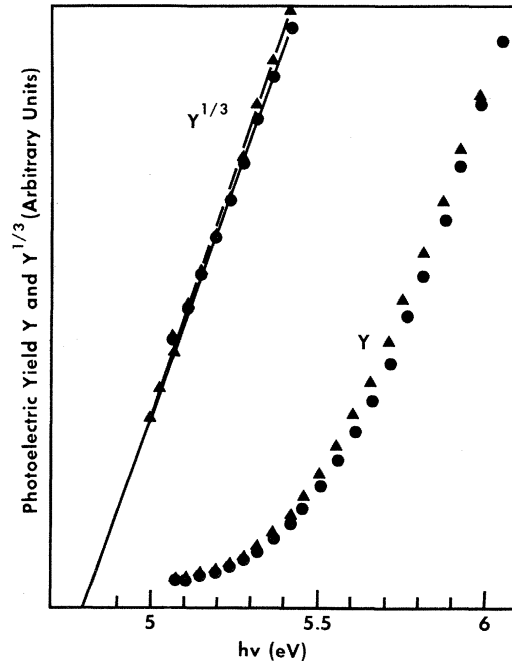


FIG. 2. Photoelectric yield Y and $Y^{1/3}$ from GaSb surfaces (circles, freshly cleaved; triangles, after 2 days).

uniform and reproducible. This finding was again verified by contact potential measurements which varied by less than 50 meV.

The high-energy extremities of the distribution give a measure of the surface potential⁵ $(E_F - E_v)_s$, i.e., the difference between the Fermi level E_F and the top of the valence band, E_v , at the surface. We observe that these high-energy ends are sharper after 2 days. We also note that they move closer to the Fermi level. Since the bulk of the material is *n* type, we conclude that the band bending becomes more uniform and larger after storage *in vacuo*.

Figure 2 shows the yield spectra $Y(h\nu)$ and the cube root of Y near threshold. We observe that the yields of the freshly cleaved and stored surface differ very little and in particular that the thresholds are equal within experimental accuracy. The threshold is equal to the ionization energy plus some constant depending on band structure and the optical excitation mechanism.⁵

The above observations lead us to conclude that the ionization energy ξ of GaSb is well defined immediately after cleavage and does not change during storage. However, the surface potential $(E_F - E_v)_s$, and hence the band bending and the work function are inhomogeneous immediately after cleavage. After storage for several days, the band bending increases and it becomes homo-

geneous. We believe that the inhomogeneities are due to local strains introduced by the cleavage and that these strains are annealed at room temperature over a period exceeding 1 day. It is not reasonable to attribute these changes to adsorption of residual gases because (1) the sticking probability of gases on cleaved III-V surfaces was found to be extremely small,⁶ (2) it would seem improbable that contamination would homogenize the band bending in two different cases, and (3) the ionization energy is not changed.

While the above described behavior is most conspicuously displayed by GaSb, it is not restricted to this substance. We have found inhomogeneous work function and band bending in *n*-type GaAs.⁴ In this case, however, no annealing was observed when the crystals were kept at room temperature. On cleaved InP surfaces,⁷ we observed unreproducible surface potential and surface-charge densities. Thus, this behavior seems quite general.

In connection with the concept of surface states, it is interesting to note that "annealing" increases the band bending and surface charge and also that samples with flat bands, i.e., *p*-type bulk in both GaSb⁸ and GaAs⁴, do not present the spatial or the temporal variations discussed above. Thus it seems that the effect of strains is to reduce the surface states or shift them towards the con-

duction band.

The fact that annealing occurs at room temperature for GaSb suggests that clean, well-defined surfaces with well-known doping and stoichiometry can probably be achieved by cleaving and heating to temperatures well below those that would cause appreciable diffusion of impurities or decomposition of the material.

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Angular Distribution of Photoelectrons Emitted from Copper Single Crystals*

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We measured the energy distribution of electrons emitted from a copper single crystal at 60° to the surface normal, using plane polarized light at normal incidence in the near uv region. Rotating the plane of polarization produced changes in the electron distribution between 5 and 28%. No such changes could be detected upon substituting a polycrystalline sample. The energy distribution of the single crystal differs considerably from that of the polycrystal. The results imply direct, *k*-conserving transitions and no scattering for a large fraction of those excited electrons which leave the crystal.

Ever since Gobeli, Allen, and Kane¹ published their pioneering work on the directional dependence of the photoemissive yield of Ge and Si crystals, the importance of similar measurement for other materials was emphasized.² The only other experimental information on the subject is obtained from photoemission electron microscopy.³ In this Letter we present the energy distribution of electrons emitted from a Cu crys-

tal and a polycrystalline Cu film for different directions of observation and different polarization and energies of the incident radiation. Furthermore, we discuss the implications of the results for the excitation and emission process.

The experimental setup is shown schematically in Fig. 1 which is drawn roughly to scale. It also indicates the orientation of the crystal. The surface of the single crystal was prepared by