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Photoelectric Determination of the Fermi Level at Amorphous Arsenic Surfaces*

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Surfaces of amorphous As exhibit photoelectric emission typical of a semiconductor. Spectral and energy distributions for electrons ejected from this material were obtained by the method of interchangeable emitters as previously applied to Te, Ge, and B. The results indicated that the Fermi level lay 0.5 ev above the top of the occupied band of electron energy states. Effects due to this energy structure were more pronounced than for the elements investigated before, but the same methods of analyzing data were applicable. The estimated density of occupied surface states in the forbidden zone was of the order of magnitude 10^{10} cm^{-2}. The work function obtained from energy data was 4.66 ev. Thermoelectric measurements showed that the samples were N-type.

P-TYPE samples of the semiconductors, Te, Ge, and B, have been studied by photoelectric techniques based on Millikan's method of interchangeable emitters.[1] As compared with metals of the same work function φ, the semiconductors emitted very few electrons having energies within a range δ of the Einstein maximum $h\nu-\varphi$. This range was correlated with the forbidden energy interval lying between the Fermi level μ and the top of the occupied band of electron energy states.

This note describes analogous experiments on amorphous As, a material previously classified only as a non-conductor.[2] Here δ turned out to be larger than for Te, Ge, or B, and the influence of the electronic energy structure was more clear-cut.

The two sealed-off photo-tubes used in this work were like those described in reference 1. Surfaces were obtained by subliming As from Pyrex refluxing chambers[3] onto Cu, Ni, Ta, or graphite. The substrates were cooler than 50°C during the depositions. Electron diffraction photographs (reflection type) showed that the layers were amorphous.[4] The pressure in both tubes was 10^{-6} mm Hg, a limit apparently set by the vapor pressure of the As. Results were tested for reproducibility on four or more separate surfaces in each tube. Other experimental details were as described in reference 1, except that the optical equipment was filled with nitrogen to prevent absorption of radiation at $h\nu=6.71$ ev.

Figure 1 shows current-voltage characteristics for As and for a typical metal having the same work function, $\varphi=4.66$ ev. Several metallic emitters were used to determine the "stopping potential at 0°K" by DuBridge's method. This reference point, $V_0=(\varphi_c-h\nu)/e$, corresponding to the coincident Fermi levels of the emitters, is marked by an arrow at -2.05 volts in the figure (here φ_c is the work function of the collector—also 4.66 ev). The curve for As approaches the axis $I=0$ tangentially and falls to unmeasurable values at a point $V_0'\sim-1.55$ volts. Thus, no detectable fraction of the electrons had energies within 0.5 ev of the Einstein maximum, $h\nu-\varphi=2.05$ ev (in contrast, almost half of those from the metal lay in this range). We conclude[1] that the As was a semiconductor with $\delta=e(V_0'-V_0)\sim0.5$ ev. More sensitive tests made at $h\nu=6.12$, 5.80, and 5.42 ev gave the same result.

Simplifying assumptions made in reference 1 led to the following expression for the energy distribution of the photoelectrons from a semiconductor: $N(\nu,E)=q(\nu)E(h\nu-\varphi-\delta-E)^m$ where q is a slowly varying function of ν. When $m=2$ and $\delta=0.53$, this relation leads to characteristics like those ob-

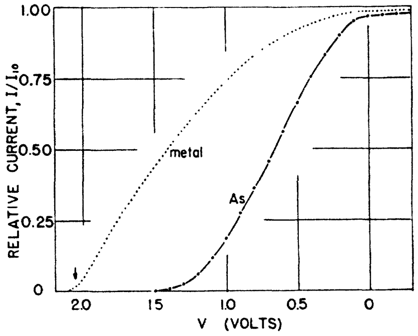

FIG. 1. Current-voltage characteristics for amorphous As and for a metallic emitter with the same work function, 4.66 ev. The arrow marks V_0, the "stopping potential for 0°K". The saturation points are at $V=0$. Currents are normalized at $V=+10$ volts. For As, $I/I_{10}=1.10$ at $V=+400$ volts. To avoid confusion, only a few of the experimental points are given. $T=300$°K; $h\nu=6.71$ ev. The abscissae should be negative.

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[1] L. Apker, E. Taft, and J. Dickey, Phys. Rev. **74**, 1462 (1948), and references given there.

[2] H. Stohr, Zeits. f. anorg. allgem. Chemie **242**, 138 (1939).

[3] Spectrographically standardized As containing traces of Sb was obtained from Johnson, Matthey and Company, Ltd. ("Matthey" Lot No. 2106). It condensed on the cool part of the first refluxing chamber, scaled off, and fell back into the hot zone. After several hours of treatment, it was sublimed through six more chambers to the photo-tube. Care was necessary to prevent tiny flakes from traveling with the vapor.

[4] See reference 2; see also C. S. Barrett, *Structure of Metals*, (McGraw-Hill Book Company, Inc., New York, 1943), and references given there. Miss Eileen Alessandrini kindly took electron diffraction data on the emitters.

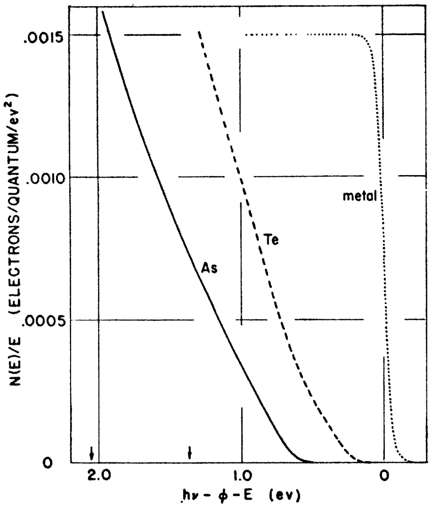

FIG. 2. $N(\nu, E)/E$ *vs.* $h\nu-\varphi-E$ for As with $h\nu=6.71$ ev. For comparison, data on crystalline Te ($\delta\sim 0.1$ ev) are shown with ordinates reduced fivefold; the arrows mark points at which $E=0$ for As (-2.05 volts) and for Te (-1.36) volts); for the latter, $h\nu=6.12$ ev. The dotted line shows the form of the Fermi function (arbitrarily normalized here at 0.0015) to which this type of plot reduces when the emitter is a simple metal at 300°K.

TABLE I. Observed yields from As and yields calculated from the relation $Y=10^{-4}$ $(h\nu-5.15)^4$ electrons/quantum.

$h\nu$	Y(obs.)	Y(calc.)
5.38 ev	3×10^{-7}	2.8×10^{-7}
5.49	1.5×10^{-6}	1.3×10^{-6}
5.70	1.5×10^{-5}	1.0×10^{-5}
6.19	1.1×10^{-4}	1.2×10^{-4}
6.71	5×10^{-4}	5.9×10^{-4}

served for As. (A discussion of the parameter m is given in the earlier paper.) As shown in Table I, the spectral distribution of the yield can be described approximately by the relation $\gamma=10^{-4}\times(h\nu-5.15)^4$ electrons/quantum, consistent with the values $m=2$ and $\delta=0.49$. Below 5.2 ev, Y was less than 10^{-7} and could not be measured, even though $h\nu$ still exceeded φ by more than 0.5 ev. Both the energy and the spectral distributions are thus indicative of the same energy structure.

The foregoing discussion is useful for comparing energy and spectral data. It is over-simplified for other purposes, however, and it involves the simultaneous determination of two adjustable parameters. The disadvantages inherent in such a procedure are obvious. A more satisfactory approach is made in Fig. 2, which shows $N(\nu, E)/E$ *versus* $h\nu-\varphi-E$ for $h\nu=6.71$ ev. In the neighborhood of $h\nu-\varphi-\delta$, this function was interpreted previously as being roughly proportional to $s(\nu, \epsilon)n(\epsilon)$. (Here s is a photoelectric excitation probability, n is the density of states, and ϵ is the energy of the electrons before excitation.) Data taken at other frequencies showed that s increased by less than a factor of two as $h\nu$ decreased from 6.71 to 5.42 ev. The variation of s with ϵ did not change form significantly in this frequency range, however, since all characteristics had the same shape. To the extent that s varies slowly with ϵ, the curve in Fig. 2 should show the same variation as the density of occupied states (plotted as a function of $\mu-\epsilon$ and averaged over the emitting area). The approach in the previous paragraph makes use of a parabolic approximation to sn when $m=2$.

These results are similar in character to those found previously for Te (see Fig. 2). They show that the "stopping potential" V_0', corresponding to the edge of the occupied band, can be as sharply defined for an amorphous material as for a crystalline one. In both cases, however, the parameter m is larger than $\frac{1}{2}$, the value which would be expected if s were independent of ϵ and if the occupied band had the normal form $n(\epsilon)\propto(\mu-\delta-\epsilon)^{\frac{1}{2}}$ near its high energy limit. (The phenomenon may be caused by fluctuations in δ over the emitting area.[1]) Thus, $N(\nu, E)/E$ is concave upward and there is some uncertainty as to the exact location of the "edge." For Te, δ is only 0.1 ev, and this effect is relatively important; for As, it is of little consequence.

In the previous work, Te, Ge, and particularly B exhibited a very small but measurable emission throughout the range $V_0<V<V_0'$ (corresponding to initial states in the forbidden zone). Surface levels with an estimated density near 10^{12} cm^{-2} were assumed as possible sources of these currents. For amorphous As, no such emission was detectable. Thus, an upper limit to photo-current originating in the forbidden band was about 10^{-8} electron/quantum, corresponding to a surface state density of the order of magnitude 10^{10} cm^{-2}.[1, 5]

Cursory examination of these As samples and of others similarly produced showed that the volume properties of the material were consistent with the results given above. The thermoelectric power ranged between 0.1 to 0.5 mv/degree at 300°K and was N-type in all cases. Resistances were about 10^7 ohms at 300°K and were an order of magnitude less at 350°K.

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[5] Since adsorbed gases may affect surface state densities, results obtained in gettered vacuum are probably not directly comparable with those found for surfaces in air by other methods (W. Shockley and G. L. Pearson, Phys. Rev. **74**, 232 (1948); see also references in the paper of footnote 1). We are indebted to Dr. J. Bardeen for a communication on this subject.