PHOTOEMISSION OF HOLES FROM METALS INTO THE ORGANIC POLYMER POLY-N-VINYL-CARBAZOLE

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Photoemission of holes from various metals into the organic polymer poly-N-vinyl-carbazole has been observed. The photoemission threshold was measured to be 1.28 eV for Au, 1.48 eV for Cu, and 1.53 eV for Al. The position of the valence-band edge relative to the vacuum level is calculated to be 6.1 ± 0.4 eV. A periodic fine structure in the spectral dependence of the quantum yield is attributed to the splitting of the electronic energy levels by molecular vibrations.

Photoemission of electrons and holes from metals into insulators has been studied in a number of inorganic systems in recent years.[1-3] These experiments allowed an independent determination of the position of the Fermi level in the metal relative to the conduction and/or valence-band edge of the insulator at the junction. Experiments have also been done on the organic crystal anthracene,[4,5] where in addition to the expected photoemission threshold, Williams and Dresner also observed a fine structure in the photoresponse which they associated with the splitting of the narrow electronic bands by molecular vibrations. In this Letter we wish to report the first results on photoemission of holes from metals into an organic polymer, poly-N-vinyl-carbazole (PVK).

Samples were made from a solution of the polymer containing 66% by weight toluene, 16% cyclohexanone, and 17% PVK. The solution was deposited onto a glass slide with transparent conductive tin-oxide coating (Nesa glass). The polymer coated slides were heated at 80°C for at least 3 h to evaporate the solvents. A semitransparent metal electrode of 0.5-cm^2 area was then evaporated onto the films. Indium-platelet pressure contact was then made over about 10% of the metal electrode while electrical contact was made to the uncoated part of the Nesa glass with a conductive silver paint. For the photoelectric measurements the samples were irradiated by monochromatic light using a Leiss prism monochromator, illuminated by a 100-W quartz-iodine lamp (FAV-Sylvania). The light-intensity calibration was made by an EP-16 junction thermopile with a quartz window. The photoemission current was measured by a Keithley-417 (fast) picoammeter and the bias was derived from a Keithley-200 dc power supply. The photocurrents measured were in the range 10^{-13} to 10^{-10} A; the high values were obtained at fields of 10^5 V/cm. Results are reported for the energy range 1.0-2.6 eV. Data were always taken using a slow electric motor drive on the monochromator drum and plotting the photocurrent directly by a Moseley X-Y recorder. The results showed no drift in the level of the dark current and each run was reproducible to ±5%. With step function illumination no fast transient could be observed. The rise time of the photocurrent varied with applied voltage, but even at the lowest applied fields only less than 10% decay could be observed after maximum was reached.

Figure 1 shows results obtained for a representative sample with an 11.5 ± 0.3 μ PVK and a 400 ± 50 Å thick gold film. Thicknesses were measured interferometrically for both materials while the thickness of PVK was also measured by capacitance technique. The results are plotted as Fowler-Nordheim plots, i.e., the square root of the quantum yield QY in arbitrary units as a function of the energy $h\nu$ of irradiation. The quantum yield per photon absorbed in the metal was obtained using reflectance and absorption data for the metal and the intensity output versus energy of the monochromator as correction

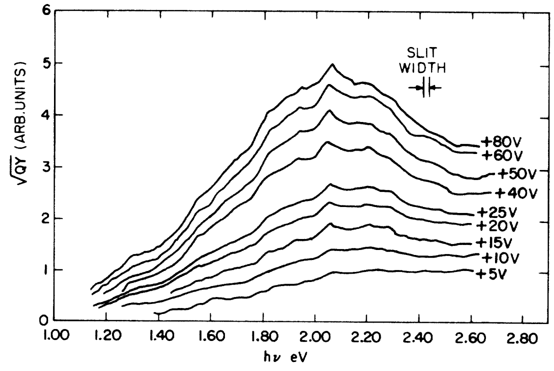

FIG. 1. Square root of the quantum yield QY (holes per absorbed electrons) versus photon energy $h\nu$ for photoemission from Au into PVK.

terms on the straight photocurrent. The figure shows curves obtained at different positive voltages, the sign of the voltage referring to the gold electrode with respect to the Nesa. Light was perpendicular to the slide, coming from the Nesa side through the PVK and finally striking the PVK-metal interface. Keeping the electric-field polarity unchanged but turning the sample 180° about an axis perpendicular to the light beam, a similar set of curves was obtained with 60% reduced absolute magnitude at 2.00 eV. When the polarity of the bias was changed, i.e., making the gold negative with respect to the Nesa, no photocurrent could be observed at energies below 1.70 eV regardless of the direction of light. The optical absorption peak of PVK due to 0-0 singlet exciton absorption is at[6] 3.57 eV; thus these low-energy photoresponses cannot be explained in terms of bulk photocarrier generation. Since the low-energy response occured only with the metal positive, it was concluded that holes are being injected from the metal into the PVK. The injection process can be fitted to a Fowler-Nordheim plot and the low-bias threshold for Au is determined to be 1.28 ± 0.02 eV. The optical absorption of Nesa glass and of Nesa glass with PVK was measured in a Cary-14 spectrophotometer. There was no detectable absorption below 3.87 eV for the glass alone while the glass with the polymer showed measurable absorption above 3.40 eV. Thus one can safely rule out carrier generation in either the Nesa or PVK in the energy range corvered by the figure. A special sample of Nesa-PVK-Nesa was measured, and it showed a very small slowly rising photoresponse in the energy range 1.7-2.6 eV. The response was, however, almost an order of magnitude smaller than for the metal-electroded sample.

The dark currents were found to be roughly Ohmic in the region 10-60 V. Similarly, the photocurrents were Ohmic at these voltages when 2.0-eV light was used. This indicates that tunneling at the interfaces and space-charge buildup in the insulator were not dominating the field dependence of the currents. An indication of current saturation with voltage was observed at 80-100 V applied.

Figure 1 also shows the shift of the photoemission threshold to lower energies with increasing bias. According to simple electrostatic theory of a well defined metal-insulator interface, the energy threshold for the emission of an electron or hole from the metal into the insulator is a function of the applied field. This Schottky lowering of the barrier is given by

$$\Delta\varphi_H = \tfrac{1}{2}(eE/\pi K\epsilon_0)^{1/2}, \tag{1}$$

where $\Delta\varphi_H$ is the change in the barrier height or threshold,[4] E is the applied field, e the electric charge, K the effective dielectric "constant," and ϵ_0 permittivity of free space. Using the threshold values from Fig. 1 and taking φ_H at 5-V bias as the value at zero field, a plot of $\Delta\varphi_H$ vs $\sqrt{E}$ yields a straight line through the origin. The dielectric constant calculated using Eq. (1) is about unity. While this value is very low,[7] Goodman[3] has obtained values between 1 and 2.15 for SiO_2 using similar analysis, where he pointed out that K may in fact be a function of the applied field. It should also be noted that large errors could be introduced by a nonlinear field distribution across the sample. Nevertheless the data do show a rough agreement with the simple Schottky-lowering model.

Photoemission measurements were also made using Cu and Al electrodes on PVK. In both of these cases photoemission of holes from the metal was observed using the previously described method of experiment and analysis. Table I summarizes the results comparing the metal work functions (φ_M) with the threshold obtained (φ_H).

It is clear from the table that φ_H does depend somewhat on the value of φ_M, and that this dependence is systematic. The variation of φ_H as a function of φ_M is less than linear, however, which indicates that surface states strongly influence the position of the Fermi level at the interface. With the above statement in mind the last column $\varphi_M + \varphi_H$ gives the position of the

Table I. The vacuum work function φ_M of various metals and the threshold energy φ_H for photoemission of holes from these metals into PVK is given together with $\varphi_M + \varphi_H$.

Metal	φ_M (eV)	φ_H (eV)	$\varphi_M + \varphi_H$ (eV)
Au	5.22[a]	1.28	6.50
Cu	4.45[b]	1.48	5.93
Al	4.20[c]	1.53	5.73

[a] E. E. Huber, Appl. Phys. Letters 8, 169 (1966).

[b] J. C. Riviere, Proc. Phys. Soc. (London), Ser. B 70, 676 (1957).

[c] A. Herrman and S. Wapher, The Oxide Coated Cathode (Chapman and Hall, Ltd., London, England, 1951).

valence-band edge in PVK relative to vacuum. The average value is 6.1 ± 0.4 eV.

The ionization potential I_C of a molecular crystal can also be calculated using classical thermodynamic parameters. I_C is given by

$$I_c = I_G - P, \tag{2}$$

where I_G is the ionization potential of the corresponding gaseous molecule and P is the energy of polarization of the crystal by a single point charge. I_G was determined by Lardon[8] to be 7.6 eV for PVK and P was estimated by Sharp[9] to be 1.5 eV for a crystal of the monomer N-isopropyl carbazole. A similar value is expected for PVK from chemical and structural considerations. Thus using Eq. (2) I_C is calculated to be 6.1 eV in excellent agreement with photoemission measurements. It should be remembered, however, that this classical calculation is an approximation for a crystal, not for the amorphous polymer.

Finally, attention should be focused on the details of the spectral response given in Fig. 1. It is easy to see that there is a well-defined fine structure at low energies which appears at all biases. A similar structure was obtained for other metals also. In order to emphasize this structure Fig. 2 shows $d(QY)^{1/2}/d(h\nu)$ for Au and Cu electrodes at 60-V bias. On account of the difference in the photoemission thresholds, the energy axes are shifted with respect to each other in order to sample the same energy range in the polymer. The structure is similar for the two metals, and the peaks are separated by an average energy 0.11 ± 0.03 eV. Molecular vibrations of organic molecules have energies typically in the range of 0.1-0.3 eV. Sharp's[9] measurements on the monomer N-isopropyl carbazole, for example, indicate that the vibrational splitting is 0.13 eV. The electronic energy bands in organic solids, however, may be an order of magnitude narrower. Interaction of electrons with molecular vibrations can therefore scatter the electron outside the band. This results in the splitting of the electronic bands into well-separated narrow bands, the energy of separation being the vibrational energy of the molecule.[4] According to theory the photoemission current follows a square-root dependence on the exciting energy only when carriers are emitted into a wide band. The observed photocurrent should show a saturation with further increase in exciting energy when the photoinjected carriers can reach all available states in the band. If instead of a wide band there are a number of narrow bands, then the resultant series of saturation effects can give rise to the observed structure. The saturation in the $(QY)^{1/2}$ at energies above 2.00 eV may be due to the exhaustion of the vibrationally split electronic levels. The observation of this fine structure implies that the width of the highest valence band in PVK must be appreciably less than 0.11 eV. In addition, experiments are now underway to study transport in this band by observing the transit of holes photoinjected into PVK from a metal electrode by a short light pulse.

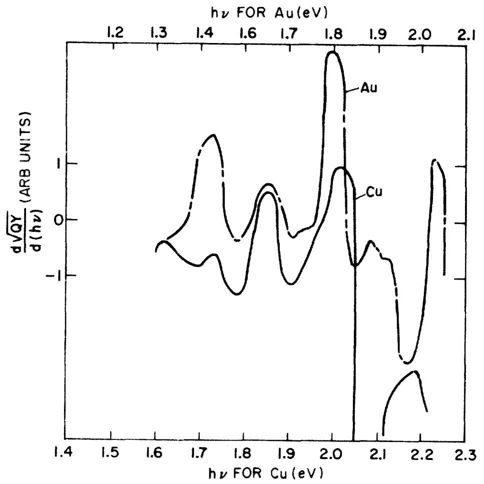

FIG. 2. Derivative with respect to energy of the square root of the quantum yield for photoemission of holes from Au and Cu into PVK.

In summary, therefore, the highest valence band of PVK with respect to vacuum level has been located, and the observation of structure on the spectral response curve has provided information on the width of this band. This knowledge together with the ability to measure the transport parameters of precisely the same band is of great value. Indeed it is felt that this combination of steady state and transient photoinjection can prove to be a tool of considerable significance in the sutdy of organic crystals and polymers.

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GALVANOMAGNETIC EFFECTS IN β-NiAl

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Anomalous behavior of the Hall coefficient and the transverse magnetoresistance was observed at liquid-He temperatures in β-NiAl which is nonmagnetic and a Hume-Rothery $\frac{3}{2}$ electron compound. A brief discussion is presented.

β-NiAl has a $B2$ structure (isotypic with CsCl) and a rather wide range of composition, 45-60 at.% Ni, about the equiatomic composition. The crystal structure and the variation of electron concentration with composition have long indicated that it might serve as an interesting material in studies of the electronic properties of metals and alloys. In this Letter we will present the anomalous behavior of the Hall coefficient and the transverse magnetoresistance at liquid-He temperatures in β-NiAl.

β-NiAl has been known as an intermetallic compound which shows a defect structure.[1] It can also be classified as a rainbow metal which shows striking color changes with variation of composition.[1,2] Optical studies have been reported recently.[2] The optical properties have been rationalized by means of a rigid-band model but are not directly associated with the defect structure. The electrical resistivity of β-NiAl has been measured at 297, 77, and 4.2°K as a function of composition.[3,4] β-NiAl is metallic but has higher electrical resistivity than aluminum by a factor of 10.

The alloys used in the Hall and magnetoresistance measurements were melted and cast under $\sim\frac{1}{5}$ atm Ar. The ingots were well annealed near their melting temperature to promote homogenization. Specimens were cut from the ingots by a Servomet spark machine into rectangular parallelpipeds with dimensions of about $1.5\times 13\times 0.5$ mm^3. After mechanical polishing the specimen had a thickness of about 0.15 mm. The specimens disignated 47.6_3 and 51.9_8 at.% Ni were cut from ingots with large grains that had resulted from efforts to utilize the Bridgman technique for the production of single crystals. These specimens contained 2-4 grains, whereas the 50.1_6 specimen was a single crystal. The other specimens were polycrystalline with an average grain diameter of about 0.5 mm. A spot-welding method was employed to make current and potential leads to the specimens using platinum wire. The Hall probes consisted of three leads to make zero output under the zero magnetic fields.

The composition of specimens was determined by chemical analyses using the nearest-neighbor portion in the ingots. Iron, which was the only transition-element impurity found, was present in the amount of $\lesssim 0.009$ at.%.

The Hall voltage was measured point by point on an X-Y recorder up to 32 kOe by a Keithley-147 nanovolt null detector. The Hall coefficient at each magnetic field was deduced from four readings (H,I), $(H,-I)$, $(-H,I)$, and $(-H,-I)$. There was a slight field dependence in the Hall coefficient which will not be discussed here. The magnitude of the change is indicated by a bar in Fig. 1.

The magnetoresistance was measured in a similar way. The constant component $I\rho(0)$ was subtracted using a Keithley-260 nanovolt source. The directions of magnetic fields and primary currents were also reversed to eliminate spurious effects. In order to investigate the effect of the magnitude of the primary current, measurements were made at currents between 0.2 and 0.5 A. No effect was observed. The dc method was employed in both measurements.

The Hall coefficient is positive between about 47 and 58 at.% Ni. The magnetoresistance is small but negative in sign except for two specimens (47.6_3 and 50.1_6 at.% Ni) at 4.2°K. At the lower temperatures of 1.75-1.79°K all the specimens showed negative magnetoresistance with a magnitude larger than that at 4.2°K. This may be