Highly electronegative metallic contacts to semiconductors using polymeric sulfur nitride*

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The Schottky barriers formed on n-ZnS and n-ZnSe by polymeric sulfur nitride have been compared to barriers formed by Au. Barrier energies as determined by photoresponse, current-voltage, and capacitance-voltage methods show that $(SN)_x$ is approximately 1.0 eV higher than Au on n-ZnS and 0.3–0.4 eV higher than Au on n-ZnSe. We believe that this is the first report of any metallic contact more electronegative than Au.

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The potential barrier that forms when a metal and semiconductor are brought into contact depends on the electronegativity of the metal.[1] When the barrier is small, the contact is said to be Ohmic. Ohmic contacts to p-type wide-band-gap semiconductors require highly electronegative metals, especially if heavy doping is not possible.[2,3] When barriers are large ($\gg kT$), contacts are said to be rectifying. On n-type semiconductors, barrier height increases with increasing metal electronegativity. Such barriers are useful for transistors,[4] for solar cells,[5] and for materials which cannot easily be made both p type and n type.[6]

The electronegativity χ of the nonreactive elemental metals commonly used to form Schottky barriers covers a range of less than 1, from 1.5 (Al) to 2.4 (Au) on the Pauling scale.[7] Sulfur and nitrogen are very electronegative insulators; however, a compound of these elements, polymeric sulfur nitride, $(SN)_x$, is a metallic conductor. The question naturally arises whether $(SN)_x$ is more electronegative than Au. In this letter we show that the effective electronegativity of $(SN)_x$, as indicated by Schottky barrier energies, is at least 0.5 higher than Au.

The source $(SN)_x$ was prepared from S_4N_4 by vacuum sublimation through silver wool held at 220°C. The resultant S_2N_2 was polymerized at room temperature followed by a 2-h treatment at 85°C in high vacuum to remove unreacted S_2N_2.[8,9] Zinc sulfide and zinc selenide crystals were heated in liquid zinc, at 880 and 750°C, respectively, to lower the zinc vacancy concentration. Net doping was n type: 5×10^{16} cm^{-3} for ZnS and 1×10^{18} cm^{-3} for ZnSe as determined by C-V data. Samples were were cleaved on opposite ends and Ohmic contacts were made using a Hg-Cd-In amalgam and heating to 450°C for 30 sec in an inert atmosphere.[10] Contact resistances were typically less than 0.04 Ω cm^2 for ZnSe and less than 2 Ω cm^2 for ZnS. The Ohmic contacts were tested for linearity and samples were cleaved again between the two contacts to expose two fresh surfaces just prior to placing in a vacuum system. Gold barriers were formed on these fresh surfaces by evaporating gold through a metal screen at about 10^{-6} Torr. Polymeric sulfur nitride barriers were deposited using a glass sublimator with the $(SN)_x$ source at 135—150°C and the sample attached to a water-cooled (15—20°C) cold finger.[11] The $(SN)_x$ diodes were isolated by scribing under a microscope.

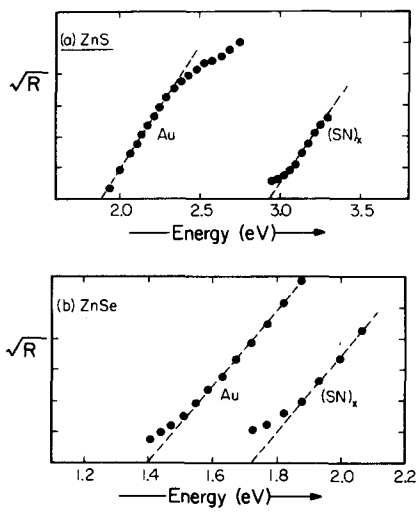

FIG. 1. Photoresponse determination of barrier energies. The square root of short-circuit photoresponse (arbitrary units) is shown as a function of photon energy for Au and $(SN)_x$ barriers on (a) n-ZnS, and (b) n-ZnSe. Dashed lines show the extrapolation used to obtain the barrier energy of each structure. $(SN)_x$ has a barrier of 2.9 eV on ZnS and 1.7 eV on ZnSe.

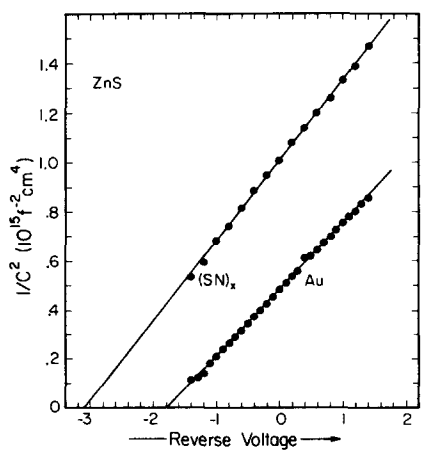

FIG. 2. Capacitance-voltage determination of barrier energies of $(SN)_x$ and Au barriers on n-ZnS. Intercept on voltage axis plus a small correction gives barrier energy.

Barriers were measured using photoresponse, current-voltage, and capacitance-voltage methods.[1] Photoresponse measurements were considered most reliable, as experience with metal barriers on various semiconductors has shown this technique to be the least susceptible to details of surface preparation. Figure 1 shows the square root of short-circuit photocurrent per incident photon plotted against photon energy for typical $(SN)_x$ barriers on ZnS and ZnSe. For comparison, the photoresponse of Au barriers is also shown. The $(SN)_x$ barrier is about 1 eV higher than Au on ZnS and about 0.3 eV higher than Au on ZnSe.

In the current-voltage measurements, the inverse slope of the logarithm of the forward current versus applied voltage for all diodes was in the range $1.2kT/q$ to $2.2kT/q$. The zero-voltage intercept was obtained by extrapolating with an inverse slope of $1.1kT/q$ from the steepest portion of the I-V curve, approximately 10^{-8}—10^{-5} A cm^{-2} for $(SN)_x$ and 10^{-3}—10^{-1} A cm^{-2} for Au. Extrapolating from the same current density for all samples would increase the $(SN)_x$ barrier energy relative to Au; extrapolating using the actual measured slope would materially decrease the $(SN)_x$ values.

The barrier energies as determined by the capacitance-voltage method for $(SN)_x$/ZnS diodes covered a wide range. This result is consistent with the formation of an interfacial layer.[12] The capacitance-voltage plot producing the lowest barrier is shown in Fig. 2. This value of barrier energy agrees with the photoresponse and I-V measurements; the value of the doping concentration obtained from the slope agrees well with the Au/ZnS barrier measurement. All C-V measurements were made in the dark, returning to zero bias in between measurements. The capacitance of the $(SN)_x$/ZnSe diodes varied only slightly with applied voltage, preventing a C-V barrier determination for this structure.

Measurements of $(SN)_x$ and Au barriers on n-CdTe were qualitatively similar to the ZnSe results, but with more scatter in the data.

Results of the various measurements are summarized in Table I. The $(SN)_x$ barriers are about 1 eV higher than Au on n-ZnS and about 0.35 eV higher than Au on n-ZnSe. The variation of the barrier energy Φ with metal electronegativity depends on the ionicity of the semiconductor.[13] The slope $S=(d\Phi/d\chi)$ is 1.0 for ZnS and 0.5 for ZnSe.[13] More recent C-V measurements[14] on chemically etched ZnSe indicate $S \simeq 0.7$. Thus, one would expect the barrier difference $\Phi[(SN)_x] - \Phi[\mathrm{Au}]$ to be smaller on ZnSe than on ZnS. The data suggest that $(SN)_x$ may be assigned an effective electronegativity of perhaps 2.9 or more on the Pauling scale, at least 0.5 higher than Au.

The $(SN)_x$ barriers exhibited ageing; for this reason, all $(SN)_x$ measurements reported here were taken within 6 h of film formation. The capacitance of some of the $(SN)_x$/ZnS diodes was dependent on the force of the 50-μm-diam Au probe used to contact the deposited layer. Capacitance increased and then decreased with increasing probe pressure. Large decreases in capacitance were caused by visible movement of the $(SN)_x$ layer on the ZnS substrate. All $(SN)_x$/ZnS measurements were made at a probe pressure corresponding to maximum capacitance; this value of capacitance was reproducible at different points on the surface of each diode.

TABLE I. Comparison of Au and $(SN)_x$ barrier energies in eV on ZnS and ZnSe substrates.

Substrate	ZnS		ZnSe	
Metallic layer	Au	$(SN)_x$	Au	$(SN)_x$
Photoresponse	1.9	2.9—3.0	1.3—1.4	1.7
I-V	1.8	2.7	1.3	1.9
C-V	1.9	3.2 (lowest)	1.6	...

In summary, we show that $(SN)_x$ is more electronegative than Au. Polymeric sulfur nitride produces barriers which are significantly larger than those produced by Au on n-type substrates. We expect that $(SN)_x$ is the first of a rather large class of very electronegative metallic-like substances which will be useful in the fabrication of heterostructure devices.

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