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Evidence for the Initiation of Copper Azide [$Cu(N_3)_2$] and Thallium Azide [TlN_3] by Carrier Emission from Schottky Barrier Contacts

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It has been reported that the initiation field $\mathscr{E}_t$ for $Cu(N_3)_2$ (*p*-type material) increases with anode metal work function while $\mathscr{E}_t$ for TlN_3 (*n*-type material) decreases with cathode metal work function. It is shown that this behavior is consistent with carrier emission from a Schottky barrier contact.

Recent work on the initiation of $Cu(N_3)_2$ and TlN_3 by the application of a voltage to metal electrodes applied to the material in the form of powders pressed into high-density pellets 0.02 cm thick has revealed that the threshold field $\mathscr{E}_t$ for initiation to occur depends on the electrode material (*1*). Three metals were examined. In order of increasing work function, they were: Zn, Cu, and W. With $Cu(N_3)_2$, it was found that $\mathscr{E}_t$ increased with increasing work function of the anode metal, and with TlN_3 it was found that both electrode metals influenced $\mathscr{E}_t$ but that the effect of the cathode metal was stronger and that $\mathscr{E}_t$ decreased with increasing work function of the cathode metal. The samples were supplied with pressure contacts. The data were compiled statistically and presented as the probability of initiation (as a percentage) as a function of the average applied field $\bar{\mathscr{E}}$ [applied voltage (V_a)/sample thickness (L)]. In the case of $Cu(N_3)_2$, the 50% initiation probabilities for Zn, Cu, and W anode materials corresponded to $\mathscr{E}$ values of 3.8×10^4, 5.0×10^4, and 6.8×10^4 V/cm, respectively, while for TlN_3, the corresponding $\bar{\mathscr{E}}$ values for the same cathode material sequence were 1.5×10^4, 1.4×10^4, and 1.1×10^4 V/cm, respectively.

This effect was associated with hole injection into the valence band in the case of $Cu(N_3)_2$, and with double injection into the valence and conduction bands in the case of TlN_3, in both cases followed by impact ionization (*1*). However, it is difficult to understand how the contact potential can play any significant role in a model based on current injection, for then (with the ohmic contacts that injection explicitly requires) current limitation is a bulk or volume phenomenon and the electrodes should play no part at all other than to provide current carriers as the volume field conditions demand (*2*). In a later publication (*3*), the Russian group also qualitatively attributes the effect to the emission of carriers into the bulk at a Schottky-type barrier contact (*4–6*), but they offer no quantitative accounting of the electrode material-dependent initiation data (*1*). Such an accounting is provided in this paper together with a discussion of the limitations of the emission model.

We consider first $Cu(N_3)_2$ and demonstrate that an increase of $\mathscr{E}_t$ with anode metal work function is consistent with a model based on the emission of holes into the valence band at a

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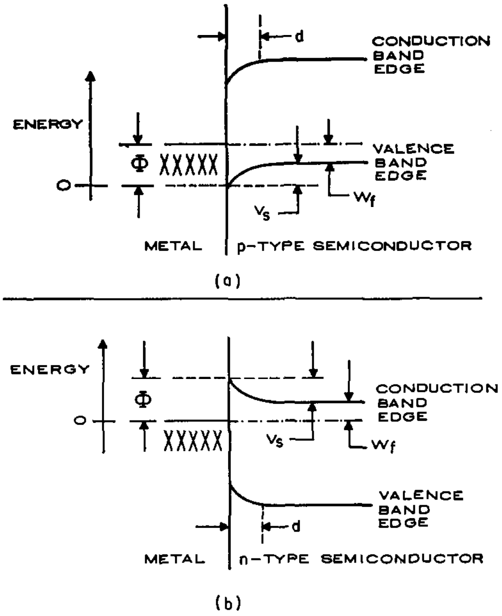
Schottky barrier contact. We view the metal–$Cu(N_3)_2$ contact as that between a metal and a *p*-type semiconductor as shown in Fig. 1a. This barrier contact is characterized by the following interrelated parameters: the barrier height Φ; the difference between the photoemission threshold Ψ of the semiconductor (the depth of the valence band below the vacuum level), and the metal work function W_m; W_f, the flat-band semiconductor Fermi energy which depends on the doping of the semiconductor; V_s, the surface potential; and *d*, the Schottky barrier thickness. In terms of these parameters the initiation experiments with $Cu(N_3)_2$ cited above reveal that the applied electric field threshold $\mathcal{E}_t$ for initiation increases with increasing metal work function.

To understand the plausibility of this result it is useful to review briefly the properties of the depletion (Schottky) barrier that results when electronic charge is exchanged between the bulk of a semiconductor and either a metal electrode or surface or interface states. The equilibrium relation for the electric field $\mathcal{E}_{s,o}$ at the semiconductor–electrode interface is (*7*, *8*):



(a)

(b)

FIG. 1. (a) Energy band diagram for the *p*-type semiconductor-metal barrier contact assumed to pertain to $Cu(N_3)_2$. Note that the barrier Φ decreases with increasing metal work function. (b) Energy band diagram for the *n*-type semiconductor-metal barrier contact assumed to pertain to TlN_3. Note that now the barrier Φ increases with increasing metal work function.

$$\mathcal{E}_{s,o}=\left[\frac{2eNV_s}{\varepsilon}\right]^{1/2} \qquad (1)$$

in practical units, where ε is the static electric permittivity of the semiconductor; *e* is the magnitude of the electronic charge; V_s is the surface potential in volts; and *N* is given by

$$N=\left[1+\left(\frac{N_A}{N_V}\right)e^{W_A/(kT)}\right]N_V e^{-W_f/(kT)}. \qquad (2)$$

where N_A is the semiconductor acceptor concentration; N_V is the effective density of states of the semiconductor valence band; W_A is the energy of the acceptors relative to the valence band edge; *k* is the Boltzmann constant; *T* is the absolute temperature and is assumed that the occupation of the acceptors is nondegenerate (*9*, *10*). Also, from the energy band diagrams of Fig. 1:

$$V_s=\Phi-W_f \qquad (3)$$

where W_f is constant for a given semiconductor material and doping. For a *p*-type semiconductor (Fig. 1a),

$$\Phi=\Psi-W_m. \qquad (4)$$

When a back-bias voltage is applied to a Schottky barrier contact, the applied voltage V_a is merely added to the surface potential V_s in Eq. (1) (*5*). With this fact and Eqs. (3) and (4), the nonequilibrium electric field $\mathcal{E}_s$ at the semiconductor–electrode interface in the presence of the applied voltage V_a is

$$\mathcal{E}_s=\left[\frac{2eN}{\varepsilon}(V_a-W_m+\Psi-W_f)\right]^{1/2}\cdot \qquad (5)$$

Eq. (5) shows that there can be a tradeoff between W_m and a threshold applied voltage $V_{a,t}$ (equivalent to an average applied electric field when scaled by the sample thickness *L*) if initiation is associated with a critical interface field $\mathcal{E}_{s,\mathrm{crit}}$. Then, the observation with *p*-type $Cu(N_3)_2$ can be understood, for as the electrode work function increases, $V_{a,t}$ must also increase to have the right-hand side of Eq. (4) remain equal to a given, constant $\mathscr{E}_{s,\mathrm{crit}}$ value.

Equation (5) shows that $V_{a,t}$ must be comparable to $\Phi = \Psi - W_M$ for the behavior just described to be apparent (W_f must be less than Φ to have a Schottky barrier). In the Russian work (*1*), $V_{a,t} = \bar{\mathscr{E}}L \simeq 2 \times 10^4 \times 0.02 \simeq 400$ V, much larger than Φ, which is of the order of a few volts at most. Thus, it would appear that the prior discussion does not apply. However, the samples were pressed pellets comprising individual powder grains that are most likely separated by potential barriers (*13*, *14*). In that event, the voltage drop across each grain, including those in contact with the electrodes, is V_a/n, where n is the number of grains in the specimen thickness L, and further, the potential drop within each grain is predominantly across the surface barriers. Thus, if the grain diameter $d \simeq 1.0$ μm (10^{-4} cm), $n \simeq 200$, and $V_{a,t}$ in Eq. (5) is about 2 V. Then $V_{a,t}$ and Φ are of the same order and the explanation proposed here for the observed effect becomes plausible. Finally, choosing the reasonable value of 10^{16} cm^{-3} for N, setting $V_{a,t} = \Phi \simeq 2$ V and neglecting W_f, Eq. (5) yields $\mathscr{E}_{s,\mathrm{crit}} = 2.2 \times 10^5$ V/cm, also a plausible value. Beyond 10^5–10^6 V/cm applied to real surfaces of wide bandgap semiconductors, destructive breakdown frequently occurs, owing to carrier emission into the bulk from interface states (*15*).

With TlN_3, it is reported (*1*) that the cathode metal is more important in influencing the initiation threshold field $\mathscr{E}_t$ and that $\mathscr{E}_t$ decreased with increasing work function of the cathode metal, essentially the opposite of the dependence observed with the work function of the anode metal electrode on $Cu(N_3)_2$. This can be understood if the metal–TlN_3 contact is viewed as a barrier-type contact between a metal and an n-type semiconductor as shown in Fig. 1b. Thus, for this type of contact,

$$\Phi = W_m - \chi \tag{6}$$

where χ is the semiconductor electron affinity (the energy separation between the bottom of the semiconductor conduction band and the vacuum level.) Using Eq. (6) instead of Eq. (4), the nonequilibrium interface field at the applied back-bias voltage V_a is

$$\mathscr{E}_s = \left[\frac{2eN}{\varepsilon}(V_a + W_m - \chi - W_f)\right]^{1/2} \tag{5a}$$

and it is clear that the smaller the electrode work function W_m, the larger the applied voltage V_a must be to achieve a given critical interface field $\mathscr{E}_{s,\mathrm{crit}} =$ constant to achieve field-initiated detonation, consistent with the observation reported for TlN_4 (*1*).

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