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Measurements of interface parameter of metal-insulator interfaces

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The interface parameter S of metal-ionic insulator interfaces was determined by measuring the photoemission thresholds of metals with a thin overlayer of ionic insulator. The results indicate S values of 1.4 ± 0.2 and 1.6 ± 0.2 for BaF_2 and LiF, respectively. These values are in agreement with the recently reported theoretical limit of 1.5.

The Schottky limit of the interface parameter S is a topic of fundamental interest. According to the existing theory of metal-semiconductor interfaces, there is a relationship between the barrier height ϕ_B and the metal electronegativity X_m. The variation of ϕ_B with the metal electronegativity can be approximated by a linear expression of the form

$$\phi_B = SX_m + \phi_0 \ , \tag{1}$$

where ϕ_0 is a constant depending only on the semiconductor.[1,2] The slope S indicates the extent to which the Fermi level can be stabilized for a given semiconductor. It has been found from the experimental studies of Schottky barriers that S is approximately zero for semiconductors with small band gaps. This observation is in agreement with the theory that these materials have high densities of interface states which "pin" the Fermi level. For materials with low densities of interface states, S appeared to have a limiting value called the Schottky limit. In previous studies, the upper limit of S was estimated to be about 1. In a recent paper, Schlüter[3] reexamined the original data on metal-semiconductor interfaces and concluded that the true Schottky limit should occur for some value between 2 and 3. However, in a more recent paper, Cohen[4] calculated $S_{\max}$ and obtained a significantly lower upper limit. Using a static dipole model, he derived an expression for S in terms of the density of interface states and the penetration length of the metal wave function into the semiconductor. With reasonable values of these quantities, Cohen estimated $S_{\max}$ to be 1.5 for large band-gap materials. Thus there is a theoretical disagreement on the upper limit of S.

In an effort to help resolve the question on the Schottky limit of the interface parameter, we have made photoemission measurements to determine the S value of metal-insulator interfaces. Various metal films with BaF_2 or LiF overlayers were investigated. The photoemission thresholds of these films were found to increase linearly with X_m. From this relationship, we were able to obtain the S value for the ionic insulator.

The photoemission measurements were made on evaporated films with dispersed radiation. The electrons in the metal film were excited with photons passing through the thin overlayer from the vacuum side. Energy distributions of the electrons photoemitted through the insulating film from the metal were measured at photon energies 7.7, 7.8, and 8.4 eV. From the widths of the energy distributions, the thresholds for photoemission from metals with thin overlayers were determined. It should be noted that the incident photons could not cause photoemission from the valence band of the insulator because the photoelectric threshold of BaF_2 or LiF is above 10 eV.[5,6] The photoelectron energy distributions were measured *in situ* immediately after evaporation at pressures lower than 3×10^{-9} Torr. The ac method was used to measure the energy distributions of the photoemitted electrons.[7]

The thickness of the BaF_2 overlayer on the metal film was estimated to be slightly more than 15 Å. This was measured by observing the photoelectric

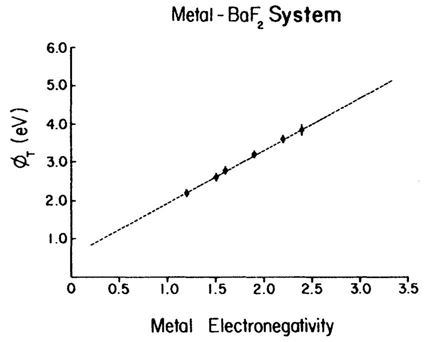

FIG. 1. Photoemission threshold ϕ_T versus metal electronegativity X_m for metals with BaF_2 overlayers. The values of X_m for Mg, Al, Cr, Ag, Pt, and Au are 1.2, 1.5, 1.6, 1.9, 2.2, and 2.4, respectively. The measured interface parameter S is 1.4 ± 0.2 for metal-BaF_2 interfaces.

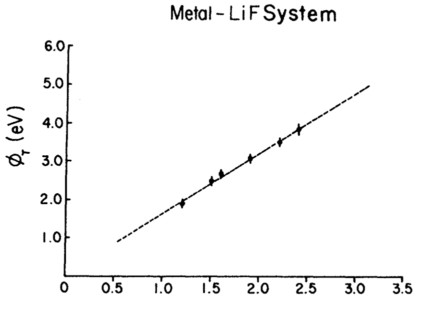

FIG. 2. Photoemission threshold ϕ_T versus metal electronegativity X_m for metals with LiF overlayers. The measured interface parameter S is 1.6 ± 0.2 for metal-LiF interfaces.

yield at 7.7 eV and the corresponding transmittance of a BaF_2 film on a LiF window at 10.2 eV for various film thicknesses. The yield was found to increase initially as the BaF_2 coverage increased. With increasing thickness of the overlayer, the yield was observed to decrease. This suggests that a significant amount of defects is probably present near the interface. These defects can cause large-angle scattering in the thin overlayer. The escape of the photoinjected electron into the vacuum would be highly unlikely if the electron is scattered back to the metal.

A thin film of BaF_2 or LiF evaporated on the metal was found to have the effect of lowering the threshold for photoemission from the metal. As shown in Figs. 1 and 2, the observed photoemission threshold increases linearly with the electronegativity of the metal. This can be explained by assuming a model described in Fig. 3. When the metal-insulator interface is formed, the photoemission threshold ϕ_T is given by $\phi_B + W$, where W is the electron affinity of the insulator. According to Eq. (1), ϕ_B can be expressed in terms of X_m. Hence we write

$$\phi_T = SX_m + W + \phi_0 \,. \tag{2}$$

Using the data we have obtained, we find that Eq. (2) fits the data with $S = 1.4 \pm 0.2$ for BaF_2 and $S = 1.6 \pm 0.2$ for LiF. The S value for BaF_2 is consistent with value[3] for SiO_2. These are ionic materials with a band gap of about 10 eV.

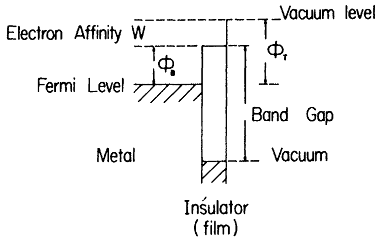

FIG. 3. Model of the metal-insulator interface.

In searching for materials that would give high S values, it is not clear whether high ionicity or large band gap is the most relevant characteristic. In the present study, we believe that both ionicity and band-gap energy of the samples are sufficiently high to provide data showing the Schottky limit or a slope close to the limit. The slightly higher S value for LiF can be attributed to a larger band gap. The gap of LiF is 13.6 eV, whereas the gap of BaF_2 is about 10 eV. According to theory,[4] the density of metal-induced interface states and the penetration length of the metal wave function into the semiconductor are expected to decrease with increasing band gap. Since the static dipole model indicates that S is inversely proportional to the product of the density of interface states and the penetration length, the larger S value for LiF is consistent with the theory. It is possible that larger S values may be obtained with ionic materials having larger band gaps than LiF. More experimental results are clearly needed to determine the true Schottky limit. However, it is interesting to note that a significant increase in band gap above 10 eV gives only a slight increase in the observed S value. Thus there appears to be a saturation of the interface parameter for large band-gap ionic solids.

In conclusion, the present results confirm Schlüter's contention that S_{max} is not 1 as previously claimed. The results also lead us to conclude that the measured S values for metal-ionic insulator interfaces are in good agreement with Cohen's theoretical limit of 1.5.

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