Heterojunctions: Definite breakdown of the electron affinity rule

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We performed a simple and straightforward synchrotron-radiation photoemission test of the electron affinity rule, the oldest and most widely used model to predict semiconductor-semiconductor band lineups. The results show, beyond any experimental uncertainty, that the rule is incorrect. The elimination of the rule and of all models related to it considerably simplifies the theoretical situation of this fundamental area of solid-state physics.

When two different semiconductors are brought together to form a heterojunction interface, the mismatch in forbidden gaps must be accommodated by discontinuities in their band edges.[1] The resulting conduction-band valence-band discontinuities, ΔE_c and ΔE_v, are the most important parameters in determining the behavior and performance of heterojunction systems. The strong fundamental and practical interest of such systems has stimulated much research to understand and predict the band discontinuities.[2] In fact, it is not clear *a priori* how the forbidden-gap difference is shared between ΔE_v and ΔE_c.

Many models have been developed to solve this problem.[3-19] Several of these models [3,4,6] are related to the so-called electron affinity rule,[3] originally proposed in 1962. This rule simply states that the conduction-band discontinuity equals the difference between the electron affinities of the two semiconductors.

For 24 years the electron affinity rule has been very popular and widely used in fundamental research and in technology.[1,2] Recently, it came under strong theoretical criticism, which prompted the development of alternate approaches.[4-19] Experimental tests of the rule have been made difficult by the chronic unreliability of the electron affinity data. The uncertainty has left this fundamental area of solid-state physics in a state of underlying confusion, which has certainly contributed to some notorious problems such as the errors in estimating the $Ga_{1-x}Al_xAs$-GaAs band lineup.

We present here a simple, straightforward, and unambiguous test of the electron affinity rule for the prototypical interface ZnSe-Ge. The test is based on synchrotron-radiation photoemission measurements of all the physical quantities involved in the rule. The results clearly demonstrate that the rule is not correct.

The experimental approach is somewhat related to that used by Zurcher and Bauer[20] to test the rule in the case of the GaAs-Ge interface. ZnSe-Ge, however, has clear advantages which eliminate the uncertainties affecting the test of Ref. 20. In particular, ΔE_v is very large for ZnSe-Ge, and therefore can be directly derived from the double-edge structure of valence-band photoemission data without relying on an indirect derivation from core-level peak data.[2] Furthermore, the large magnitude of the discontinuity enhances the discrepancy between the predictions of the rule and the experimental findings, to values well beyond any reasonable experimental uncertainty.

The simple philosophy of the test is explained by Fig. 1. Here DOS labels the density of states of a semiconductor in the energy region close to its forbidden gap, E_g. E_v and E_c are the band edges. The distance between E_c and the vacuum level (VL) is by definition the electron affinity, χ. EDC labels the energy distribution curve of photoelectrons emitted by the semiconductor under bombardment by photons of energy $h\nu$. The shaded area corresponds to the secondary electrons created by inelastic scattering processes. The low-energy cutoff of the distribution corresponds to the vacuum level. The upper edge corresponds to $E_v + h\nu$.

The distance in energy between the two EDC edges D equals $h\nu - (E_g + \chi)$. Thus, the electron affinity can be directly derived from the EDC spectra. Calling D_1 and D_2 the values of D for two different semiconductors, the electron affinity rule for their interface trivially predicts that

$$\Delta E_v = D_1 - D_2 \ . \tag{1}$$

Equation (1) can be used to directly test the rule with photoemission methods. This is done by comparing the value of ΔE_v predicted by Eq. (1) with the measured discontinuity. In turn, the discontinuity is measured[2,21-23] by taking EDC's on thin overlayers of one semiconductor deposited on the other. This approach has been discussed in detail in several recent reviews.[2]

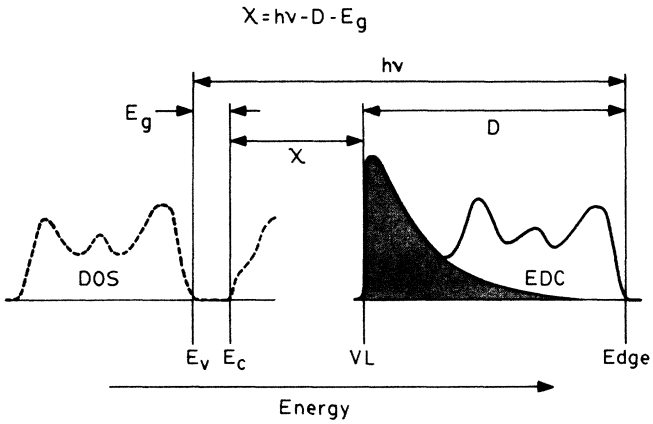

FIG. 1. Schematic explanation of the test. The distance in energy D between the upper and lower edge of a photoemission spectrum is related to the electron affinity. For a detailed explanation, see text.

The above approach is not immune from experimental difficulties. The low-energy EDC cutoff can be due to the electron analyzer rather than to the sample vacuum level. This problem is solved by electrostatically biasing the sample to move the low-energy cutoff of its spectra to higher energies. The sample can become charged when exposed to the electron beam, and this affects the EDC's. However, charging problems are easily corrected by illuminating the sample with an intense visible light which generates photoconductivity. Of course, the results are crucially dependent on the cleanliness of the system and the test must be performed *in situ* under ultrahigh-vacuum conditions.

ZnSe-Ge offers the additional advantage of being a very extensively studied interface.[21-24] Several photoemission experiments measured ΔE_v,[21-23] with results between 1.29 and 1.52 eV. In the present case, from double-edge spectra like the two top EDC's of Fig. 2, we derive $\Delta E_v = 1.44$ eV. These curves were taken on as-grown Ge overlayers on cleaved ZnSe. Extensive experiments have demonstrated that the discontinuity measured at these Ge thicknesses coincides with the final ΔE_v for very thick overlayers.[22] Furthermore, they also demonstrated that ΔE_v does not change (within 0.1 eV at most) in going from disordered to ordered overlayers.[21]

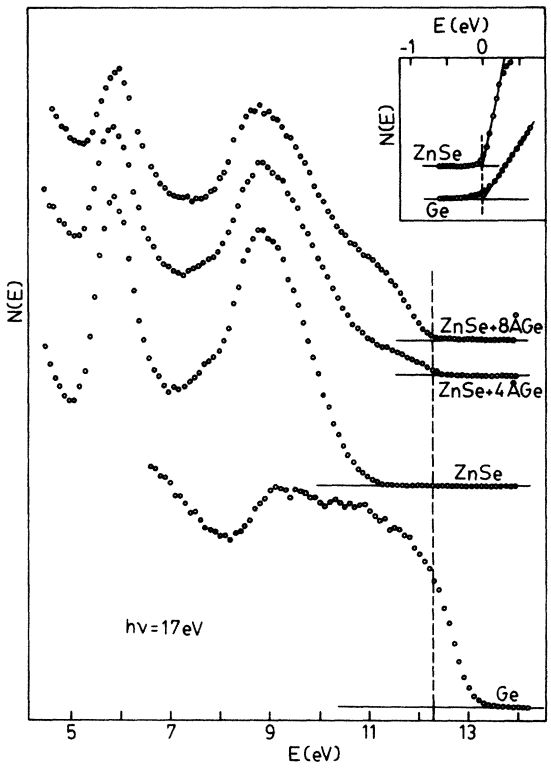

FIG. 2. A direct illustration of the breakdown of the electron affinity rule. The two upper curves are photoemission spectra taken on ZnSe covered by 4 and 8 Å of Ge. They exhibit the characteristic double edge due to the valence-band discontinuity. The two other curves refer to clean ZnSe and Ge. These last two curves were aligned to each other so that the low-energy cutoffs coincide (see inset). The two upper curves were aligned with respect to the ZnSe curve so that the bulk-ZnSe features coincide. Thus, the electron affinity rule would predict that their upper edges coincide with the upper edge of the lower Ge curve. The dashed line emphasizes that this prediction is wrong.

Measurements of the distances D for ZnSe substrates and very thick (>50 Å) Ge overlayers were performed on six different systems, with three different photon energies, $h\nu = 17$, 20, and 23 eV, and with a variety of bias voltages and intensities of the discharging light. The combined results of all these measurements give $D_1 - D_2 = 2.21$ eV. This value is 0.77 eV larger than the experimental valence-band discontinuity.

This complete breakdown of the electron affinity rule is directly visualized in Fig. 2. The two bottom curves show the EDC's of ZnSe and Ge, aligned with respect to each other so that their low-energy cutoffs coincide (as shown in the inset). The two top curves have been aligned with respect to the clean-ZnSe EDC so that the ZnSe-related features coincide (e.g., the Zn $3d$ peak). Thus, if the electron affinity rule was valid, the upper edges of the two top curves would coincide with the upper edge of the Ge EDC. The dashed vertical line shows that they do not, and dramatically so.

Of course, the validity of this test depends on its combined accuracy. Contributing to this accuracy are the uncertainty in deriving the edge positions from the experimental curves, and the uncertainty in measuring ΔE_v.[2] From the extensive experiments performed by different authors on this interface,[21-23] we can derive a conservative uncertainty for our present ΔE_v value, $1.44^{+0.08}_{-0.15}$ eV. The combined uncertainties in deriving the four required edge positions give an uncertainty of the order of 0.4 eV for $D_1 - D_2$. This is consistent with the standard deviation of our $D_1 - D_2$ data, 0.46 eV. Thus, in the worst case there is still a large difference of 0.24 eV between the minimum possible value of $D_1 - D_2$, 1.76 eV and the maximum possible value of ΔE_v, 1.52 eV.

We emphasize that our test has several self-consistency features which increase its reliability. For example, one could argue that we are not really measuring the electron affinity of Ge, but that of whatever species we obtain by depositing Ge on ZnSe. However, the electron affinities which must be used for the electron affinity rule are specifically those of the interface species.[6] Thus, we are measuring exactly the quantities which are relevant for the rule. As a limit case, the test would be valid even if our system was heavily contaminated—which it was not. The EDC's taken at low Ge coverage are affected by signal related to localized states.[24] However, this is irrelevant to the huge discrepancy between the upper edge of the two top curves of Fig. 2 and of the bottom curve.

This result should put an end to a long and bitter controversy, and simplify the theoretical situation by eliminating one class of models. Obviously, it does not *per se* endorse a specific alternate model. For example, in the framework of Mailhiot-Duke approach,[4] it can be interpreted as evidence that there is substantial relaxation of the interface atomic positions with respect to their bulk values.

We emphasize, however, that recent evidence was provided for a correlation between Schottky barrier heights and heterojunction valence-band discontinuities.[2,25] This

result could either be explained[25] by the midgap-energy approach proposed by Tersoff,[16,26] or by a combination of the electron affinity rule and of the Schottky model for metal-semiconductor interfaces. The breakdown of the electron affinity rule leaves Tersoff's approach[16] as the only heterojunction model consistent with all present experimental data.

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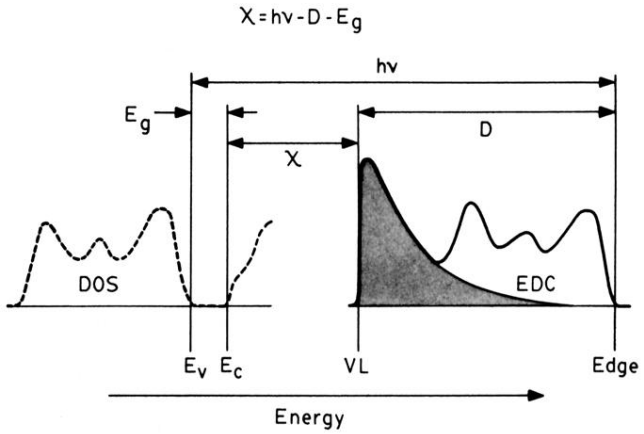

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