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Duality in Fermi-level pinning at Cu/InP(110) and Ag/InP(110) interfaces

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Fermi-level movement and interfacial chemistry for room-temperature and 80-K low-temperature Ag/InP(110) and Cu/InP(110) have been examined by use of photoelectron spectroscopy. Two different pinning positions (0.95 and 0.7 eV above the valence-band maximum), which are associated with either defects or metal-induced gap states (MIGS), are well correlated with the interfacial reaction. These results indicate that both MIGS and defects can pin the Fermi level and that the interplay between them should be taken into account.

Understanding the physical nature of Schottky-barrier formation at metal-semiconductor interfaces is of considerable interest. Among the numerous models proposed in recent years, two have attracted the most attention, namely, the defect model[1] and the metal-induced gap-states' (MIGS) model.[2] Despite the previous point of view that one mechanism is solely responsible for Schottky-barrier formation, which has proved unacceptable, efforts have been devoted to unify the two, such as the work done by Zhang *et al.*[3] and Mönch.[4] However, in general the nonidealities of the real interfaces make experimental distinction extremely difficult. Fortunately, recent studies of metal-GaAs interfaces have revealed that the temperature at which the interfaces are prepared can be used to control the interfacial processes. These studies have provided valuable information pertinent to the physical nature of the Schottky-barrier formation.[5,6] In this report, through a study of two prototypical interfaces, Ag/InP(110) and Cu/InP(110) at room temperature (RT) and 80 K low temperature (LT), for the first time we provide unambiguous experimental evidence and establish direct correlation between the interfacial chemistry as well as interface perfection with Schottky-barrier formation. In particular, instead of single mechanism explanation this work shows that the Fermi level can be pinned by both defects and MIGS. Furthermore, the ultimate Schottky-barrier formation depends on the interplay of the two mechanisms which can be controlled through a change of interface growth temperature. The results of this work support the previous theoretical investigation.[3]

Ag/InP and Cu/InP interfaces were prepared by cleaving InP crystals in the (110) orientation, followed by metal deposition. All the preparations and measurements were done inside a standard ultrahigh vacuum chamber with the samples held at either RT or 80 K LT. The chamber pressure was in the 10^{-11} torr range. Sn-doped n-type InP and Zn-doped p-type InP single crystals of doping 5×10^{17} cm^{-3} were acquired from Crysta Comm Inc. The photoelectron-spectroscopy (PES) study was performed at the Stanford Electronics Laboratories with a monochromatic He discharge lamp. The metal coverage range spans 4 orders of magnitude [0.001—10 monolayer (ML): 1 ML$=8.4\times10^{14}$ atoms/cm^2 on the InP(110) surface]. In the low-coverage regime, a specially designed evaporator was used with the metal sources 1.5 m from the sample surfaces. This distance minimizes the heating of the sample surface during the metal deposition and provides accurate coverage. Photoemission core-level ($h\nu=40.8$ eV) and valence-band ($h\nu=21.2$ eV) spectra were recorded after cleaving and after each step of metal deposition.

Figure 1 presents a set of photoemission core-level (In $4d$) spectra of Cu/p-InP at both RT and LT at the selected Cu coverages. All the spectra are decomposed into surface (s), bulk (b), and reacted (r) components with a computer curve fitting routine. In this analysis spin-orbit splitting of 0.86 eV for In $4d$ and a statistical branching ratio 1.5 were used. The Lorentzian linewidth for the bulk component used is 0.23 ± 0.1 eV, consistent with that used for other metal-InP interfaces.[7] This width was fixed during the whole fitting process. The separation between the bulk and surface components is found as 0.35 ± 0.1 eV. Since the bulk component is the dominating feature in the spectra we find that the uncertainty of the bulk component position is less than 0.05 eV after trying different fitting parameters. This uncertainty, as we will discuss later, will not affect our major conclusion.

The substrate band bending is measured by the bulk component shift, which is also consistent with the shift of the valence-band spectra (for brevity the spectra are not shown here) at low-metal coverages. The reacted component on the high kinetic-energy (KE) side of the main peak has been identified as elemental In segregated to the Cu surface.[8] This is considered as a fingerprint that a reaction between the deposited metal and InP is taking place. The reaction is detected around 0.3 ML Cu coverage. Comparing the spectra taken at the Cu/InP interfaces at the two temperatures, we find that the interfacial reaction and the substrate band bending is only influenced slightly by the temperature. The major differences between the two interfaces reflected from the spectra are the substrate signal intensity attenuation rate and the energy position of the reacted component. In a detailed study, both of these are attributed to the temperature dependence of the overlayer morphology, that is, three-dimensional cluster formation at RT and a much more uniform overlayer at LT.[9]

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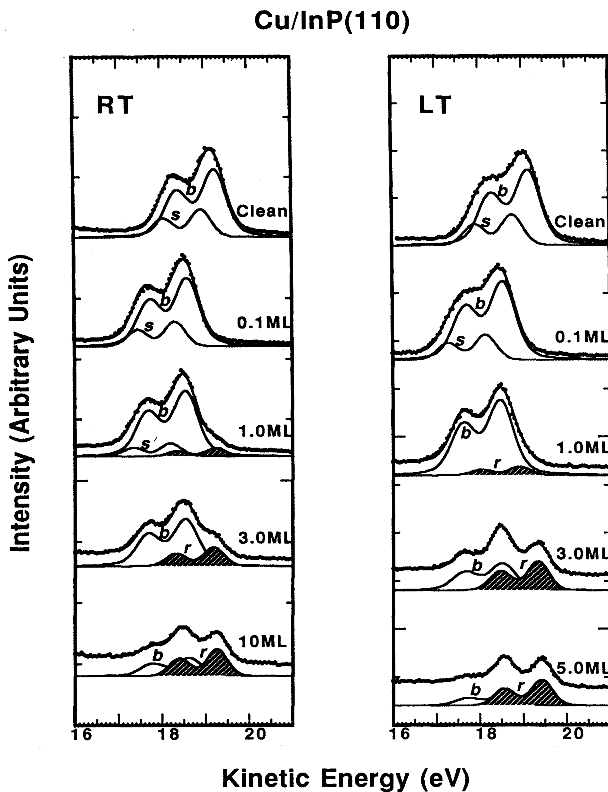

FIG. 1. PES In 4d core-levels spectra ($h\nu$=40.8 eV) of RT and 80 K LT Cu/InP(110) interfaces at selected Cu coverages (in ML). A computer routine was used to separate surface (s) and bulk (b) components from the InP substrate as well as the reacted component (r) due to the interfacial reaction.

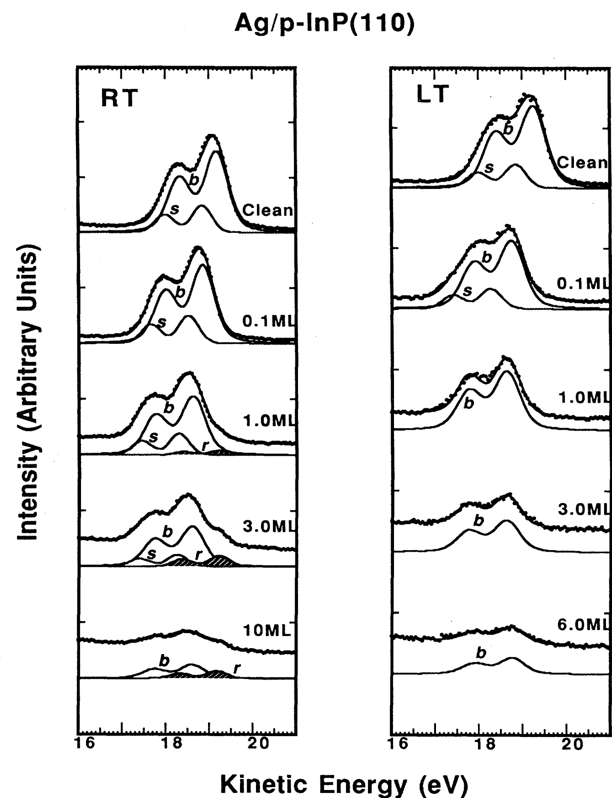

FIG. 2. PES In 4d core-level spectra ($h\nu$=40.8 eV) of RT and 80 K LT Ag/InP(110) interfaces at selected Ag coverages (in ML). A computer routine was used to separate surface (s) and bulk (b) components from the InP substrate as well as the reacted component (r) due to interfacial reaction. Notice the reacted component disappears at LT.

The decomposed In 4d spectra of the RT and LT Ag/InP are shown in Fig. 2. A reaction between Ag and InP is detected at the RT interface clearly shown by a shoulder on the high KE side of the main peak even in the raw data. This is consistent with a previous study.[10] Unlike Cu/InP, a strong temperature dependence on the Ag/InP interfacial properties is clearly seen when one compares the spectra taken at RT and LT. In addition to the fast attenuation of the substrate signal intensity, which implies a similar change of the overlayer morphology as the Cu/InP case, the most profound change is the disappearance of the reacted component at LT. This indicates that the interface reaction is largely, if not completely, suppressed at the reduced temperature, a common phenomenon at metal-GaAs interfaces.[5,6] As we will discuss later, it is the change in the interfacial recation that leads to a drastic change of the Fermi-level pinning at this interface. Similar studies have also been performed for n-type InP for two interfaces and two temperatures. As expected the overlayer morphology and the interfacial chemistry as well as their temperature dependence are the same as the p-type InP.

The evolution of the InP surface Fermi-level positions is illustrated in Fig. 3 for n- and p-type InP covered by Cu and Ag at both RT and LT. At RT, Ag/InP (top panel) and Cu/InP (bottom panel) give similar Fermi-level movement patterns, which are typical for a number of metal-InP interfaces. The Fermi levels progressively move toward the upper midgap with increasing metal coverage, and they are finally pinned in a narrow range around 0.95 eV above the valence-band maximum (VBM) for both n- and p-type InP. The interesting finding is the difference in pinning behavior between these two LT interfaces. The overall Fermi-level pinning pattern for Cu/InP at LT does not show appreciable change with respect to that at RT. The same final-pinning position as that at RT is observed for both n- and p-type InP. On the other hand, an important change in the Fermi-level pinning is found at the LT Ag/InP interface. The final Fermi-level pinning position is at 0.7 eV above the VBM for both n- and p-type InP, that is about 0.25 eV below that at RT. We are confident about these results since the separation is much larger than the experimental uncertainty. Moreover, in this figure the Fermi-level positions upon warming of the LT Cu and Ag/n-InP interfaces to RT are shown. Cu/InP does not show a large change in the interfacial chemistry as well as the pinning position. In contrast, the pinning position of the Ag/InP moves from its LT position to its RT position accom-

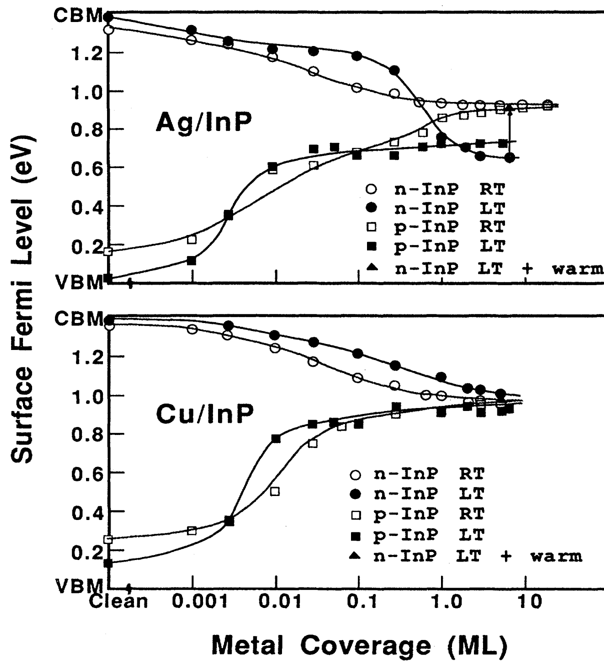

FIG. 3. Band-bending diagrams for Ag/InP(110) (top panel) and Cu/InP(110) (bottom panel) at RT and LT. The Fermi-level motion shows a similar pattern for RT Ag/InP and RT and LT Cu/InP but a strikingly different pattern for LT Ag/InP, suggesting that different mechanisms are responsible for the Fermi-level pinning.

panied by the reappearance of the interfacial reaction.

The relationship between the chemical reaction and the Fermi-level pinning at the metal-InP interface appears to be critical. In particular, it is found that two different pinning positions depend on whether or not interfacial chemical reactions have taken place. For RT Ag/InP as well as RT and LT Cu/InP, a reaction is seen and the pinning position at 0.95 eV above the VBM is observed. In contrast, for LT Ag/InP no reaction is detected, and a pinning position of 0.7 eV above the VBM is found. The movement of the Fermi level with metal coverage is similar for the three reactive cases but is strikingly different for the nonreactive case, suggesting different pinning mechanisms operating there.

The data can be interpreted using two mechanisms in which the Fermi level is pinned by interface states. The defect model[1] ascribes these interface states to intrinsic defects of the semiconductor, for instance, antisite defects. The defects could be generated during interfacial reaction and/or semiconductor surface disruption. The MIGS model[2] considers the interface states resulting from metal wave functions tailing into the semiconductor. In this case the presence of intrinsic defects is not necessary. For InP theoretically and experimentally it has been proven that the pinning position associated with defects is around 0.95 eV above the VBM;[11–13] whereas the pinning position theoretically predicted for MIGS is around 0.76 eV above the VBM.[14]

Since the pinning positions due to defects and MIGS are far away from each other, it is possible to make unambiguous experimental distinction between the two mechanisms. In this regard InP offers a better example than other semiconductors where the pinning positions due to the two mechanisms overlap with each other.[1,14] In this work interfacial reaction and InP surface disturbance is observed for RT Cu, and Ag/InP as well as LT Cu/InP interfaces and the 0.95-eV pinning position indicates that the pinning is due to the defects. PES and electrical measurement have also been performed for a wide range of metals on InP(110) at RT by Newman *et al.*[15] They found that the majority of metal-InP interfaces are imperfect with the pinning positions falling in a range of 0.95 ± 0.1 eV above the VBM. Defects are suggested to be responsible for the Fermi-level pinning at these interfaces. In contrast, the reaction is largely suppressed at the LT Ag/InP interface, and in turn, much fewer defects are expected. This implies that MIGS can play a dominant role in the Fermi-level pinning. In fact, the coincidence of the pinning position at this interface with the predicted position by the MIGS reinforces our argument.

It is interesting to compare our RT pinning positions with those in the literature. Using photoemission spectroscopy 0.9 and 0.7 eV were found for Ag and Cu, respectively, on *n*-type InP by both Brillson *et al.*[16] and our group.[15,17] The present results are the first measurements using both *n*- and *p*-type InP in the same experiment. This removes some of the uncertainties involved in the photoemission measurement. Due to this and additional work we have done, we are now convinced that the 0.95-eV pinning position is correct for the Cu/InP reported here. *I*-*V* measurements for thick (~1000 Å) Cu on *n*-type InP also give a value of 0.92 eV.[15] However, for Ag, a value of 0.8 eV was obtained for the thick overlayer,[15,17] suggesting that MIGS as well as defects may be important for the thick metal overlayer, possibly because an increasing metal screening reduces the effect of defects.

Our key result is the different pinning positions (0.95 to 0.7 eV above the VBM) at the Ag/InP interface at two temperatures. The one-to-one correlation between the different behavior of interfacial chemistry and pinning mechanisms is established. Both defects and MIGS can pin the Fermi level. The data is dramatically different from the previous single mechanism explanation. More importantly, the MIGS can be operative when the semiconductor surface is covered by a thick uniform metal overlayer, and defects will be created when the semiconductor surface is disturbed. Thus, the different pinning behavior at the LT Ag/InP as compared with other interfaces studied could be viewed as the competition between two parallel mechanisms. In the case of Ag/InP, interfacial chemistry is suppressed at LT, and MIGS seem dominant. Here we associate the suppression of chemistry with a reduction of defect formation. On the other hand, for Cu/InP the interfacial reaction is not significantly influenced by the temperature, nor, we infer, is the defect formation, and MIGS do not seem important. The key point here is that the relative density of defects versus

MIGS determines which mechanism will be dominant. Through their calculation, Zhang *et al.*[3] concluded that if the defect density is too high, they cannot be completely screened out by MIGS, and can still play a dominant role. Our results are consistent with their conclusion. The interplay between the two mechanisms was briefly discussed before for metal-InP cases.[18] Here we provide a clearcut experimental evidence that both mechanisms, which are closely correlated with the interfacial reaction, can be operative. Moreover, we believe that the temperature-dependence study of the metal-InP interfaces can be used as a guide line for investigation of Schottky-barrier formation at other metal-semiconductor interfaces.

In conclusion, we propose that both defect and MIGS mechanisms can play an important role in the Fermi-level pinning at metal-InP(110) interfaces. For MIGS to be dominant, it appears necessary to reduce defect formation to a sufficiently low level.

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