Applied Surface Science 65/66 (1993) 789–794
North-Holland

applied
surface science

Search for photoinduced dipoles at heterojunction interfaces

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Received 29 June 1992; accepted for publication 5 August 1992

We tried to apply the mechanism of surface photovoltage (SPV) to a particular class of semiconductor heterojunctions, those having staggered gaps, with the aim of photoinducing charges of opposite sign at the interface notches and of creating a dipole that modifies the band discontinuities.

We performed photoemission experiments at room temperature and at low temperature on the Si/InP(110) heterojunction for a thin coverage of silicon on n-doped and p-doped InP substrates. We found a shift of all the electronic features (both from Si and from InP) to higher binding energies at low temperature when using the n-type InP. No shifts were observed for p-type InP, where we expected to find a photoinduced interface dipole and a consequent shift in opposite directions of Si and InP structures. The implications of these results are discussed.

1. Introduction

The physical origin of semiconductor band discontinuities in heterojunctions is a very interesting field of research in current solid state physics [1]. This interest originates from the fact that the transport properties of such systems are mainly determined by the value of the discontinuities. An accurate knowledge of the mechanisms which contributes to the final value of the discontinuity, and the possibility to tailor this value is therefore very attractive for people working in the semiconductor devices engineering.

In the past years theoretical [2,3] and experimental [4–7] works have demonstrated the possibility to modify the band discontinuities introducing thin layers of different materials between the two semiconductors which form the heterojunction. More recently, the same result was obtained through the deposition of two layers of materials of different electronegativity between the two sides of a homojunction [8,9]. These effects were both explained in terms of the formation of electrostatic dipoles at the interface [4,10].

Recent studies on a non-equilibrium effect in Schottky barriers, known as surface photovoltage (SPV) [11–16], have suggested that staggered gaps heterojunctions could be good systems to create an interface photoinduced dipole, and therefore to change the band offsets, without resort to intralayers deposition.

In these systems [1] the valence band and the conduction band discontinuities have opposite sign. Under particular doping and temperature

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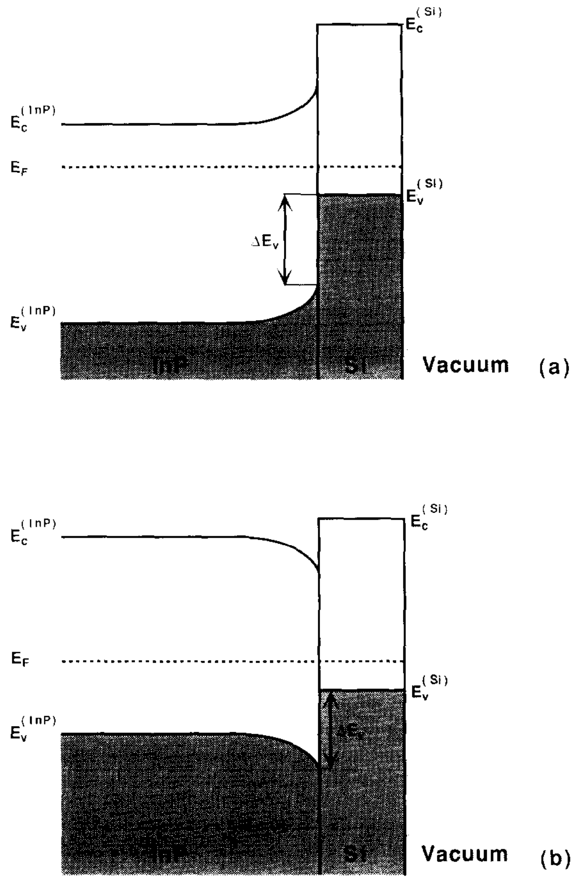

Fig. 1. Band structure of the Si/n-InP(110) (a) and Si/p-InP(110) (b) interfaces. At equilibrium the Fermi levels of InP and Si are aligned, and the InP bands are bent in opposite ways in the two cases. The x axis is not in scale, i.e., the InP depletion layer is more than 100 Å wide, while the Si layer is 10 Å thick. The band discontinuity ΔE_v (0.6–0.7 eV) is shown in the figures.

conditions, lighting the system, one can store charges of opposite sign at the two sides of the junction, thus creating the electrostatic dipole.

Examples of staggered gaps heterojunctions are those of figs. 1 and 2.

We used in our experiments Si/n-InP and Si/p-InP heterojunctions (figs. 1a and 1b). From core level analysis [17] we found for the valence band discontinuity (shown in figures as ΔE_v) of this system the value 0.6 eV. Previous results report 0.57 [18] and 0.56 eV [19] at room temperature. The values of the two semiconductors band gaps differ of only about 0.2 eV, so that the conduction band minimum of silicon is shallower than the InP one: this is a typical staggered gaps situation.

The behavior of Si/n-InP system under synchrotron radiation illumination is very simple to explain (see fig. 2a). Photons impinging on the sample can excite a great number of electron–hole pairs. Electrons in the conduction band are driven away from the interface region by the built in potential of the depletion layer. We will refer to this electron flux as to photocurrent. Holes in the valence band are driven to the thin Si layer where they are trapped. There are several other contributions to the total current to restore charge equilibrium. The main processes are thermionic current and recombination through gap states at the interface. At low temperature the efficiency of the restoring processes is not sufficient to compensate the charge separation due to the bulk potential. As in the experiments on the Schottky barrier the result is an accumulation of holes that reduces the band bending [11–15]. The main difference between the two cases is that in our system the positive charges are stored in the potential well between the junction and the vacuum while in the Schottky barriers the holes are trapped in the depletion region of the semiconductor near the junction with the metal. The band flattening which occurs at low temperature is not evidenced in fig. 2a.

In the Si/p-InP system, the band configuration is different, due to the fact that the gaps are staggered; this gives rise to two potential "notches", as represented in fig. 2b. The two notches, one on the InP side and the other on the Si side, can trap electrons and holes under illumination. In this case there is another contribution to the restoring process, i.e., the tunneling current. When the temperature is sufficiently low, i.e., the restoring current is less than the photocurrent, we expect to find a net charge separation, and thus an induced electrostatic interface dipole. The Si valence band maximum should move to higher binding energies, while the InP VBM should move in the opposite direction. This should give a reduction of the valence band discontinuity, possibly dependent on the sample temperature.

2. Experimental details

Photoemission experiments were carried out at the Mark V beamline of the Synchrotron Radiation Center in Madison WI. The beamline is equipped with a Grasshopper monochromator and a cylindrical mirror analyzer (CMA).

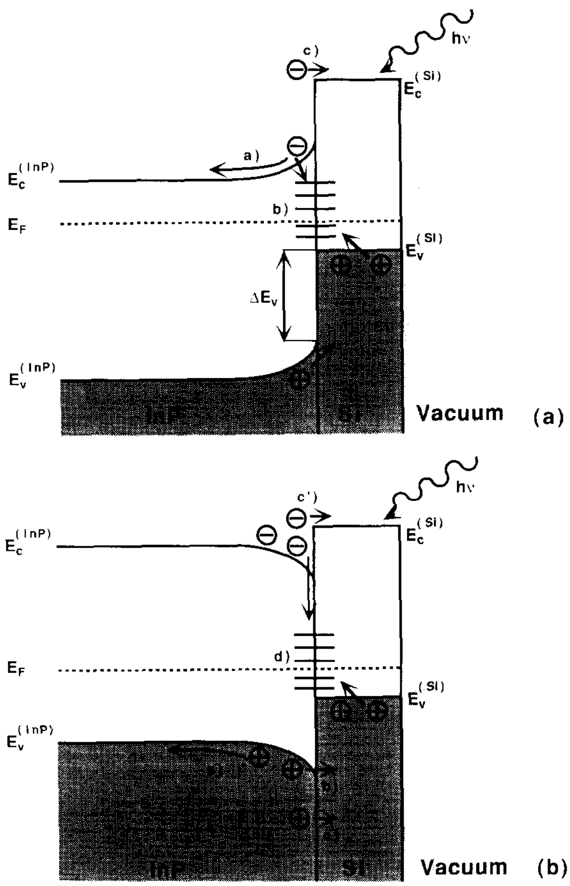

Fig. 2. Si/n-InP interface (a) and Si/p-InP interface (b) during UV irradiation. (a) Electrons, excited in the conduction band, are driven away – photocurrent, path a –. At room temperature equilibrium is restored via recombination processes and via the thermionic current – respectively processes b and c – and no stored charge is present. At low temperature the photocurrent is greater than the restoring current. The accumulation of positive charge arising at the right side of the interface reduces the band bending (not shown in the figure). (b) At room temperature different mechanisms restore charge equilibrium: tunneling current – path b –, thermionic current – c and c′ – and recombination process – d –. Holes on the Si side and electrons on the InP side can be trapped at the interface by the potential "notches".

Photon-energy ranged between 38 and 200 eV. Overall energy resolution was estimated from the broadening of the Fermi level and ranged between 0.2 and 0.3 eV. Samples were cut from commercial n-doped and p-doped ($\delta = 4 \times 10^{18}$–$1.6 \times 10^{19}$ cm^{-3}) InP(110) bulks. The InP surfaces were cleaved in situ under UHV conditions (operating pressure was 5×10^{-10} mbar). Si was deposited on the InP clean surface at room temperature and the evaporation was achieved heating directly the Si bulk by Joule effect. After deposition the system was cooled to 120 K using a liquid helium device.

3. Results and discussion

3.1. Si / n-InP

In fig. 3 the valence band and the core levels for the Si/ n-InP interface taken at room temperature (RT) and at low temperature (120 K) are shown. At 120 K all the spectra features are shifted of 0.3 eV to higher binding energies. A scheme of the mechanism responsible for this effect is shown in figs. 1a and in 2a which represent the Si/ n-InP junction at equilibrium before light illumination, and during the UV irradiation of the system. At equilibrium the Fermi levels of the two semiconductors are aligned, and the InP bands are bent (see fig. 1a). On the Si side we assume that the bands are flat because of the extremely small thickness (10 Å) of the silicon layer. According to previous works, we assume that the silicon layer is amorphous and slightly p-doped [20]. The InP depletion region is about 1000 Å wide. Note that, for simplicity, the x scale in the figure is not the same on both sides of the junction. In the non-equilibrium case, photons irradiate the semiconductors and the electrons excited by the light jump in the conduction band leaving holes in the valence band. Here electrons are swept away from the junction by the bulk potential giving the photocurrent (path a in fig. 2a). At room temperature there are several mechanisms that can restore the photocurrent: path b of fig. 2a shows the recombination process while path c is the thermionic current. The magnitude of the total restoring current and of the photocurrent is of the same entity at room temperature and there is not any change in the band bending with or without illumination. When the temperature is decreased the photocurrent acts in the same way: excited electrons in conduction band are driven away by the InP potential. The holes, left in the valence band, due to the potential, remain trapped between the junction and the vacuum. Electrons and holes created in the Si side have the same behavior. The recombination effects and the thermionic current are less effective at low temperature while the photocurrent remains unchanged. The result is an accumulation of positive charge in the potential well on the Si side. The stored holes reduce the band bending and we can see the total shift of the spectra of higher binding energies (lower kinetic energies). This is the same effect found in the SPV experiments on the Schottky barrier and it is consistent with previous results on CdTe/n-GaAs(110) heterojunction [21]. It should be noticed that the intensity of the effect is temperature depending; at 180 K the spectra (not shown) show a shift of about 0.2 eV.

3.2. Si/p-InP

Fig. 4 shows data taken at room temperature (open circles) and at 120 K (full circles) for the Si/p-InP system. We report only the valence band and the Si core level but all the other structures have the same behavior. It is clear from the spectra that there is no shift at 120 K. Figs. 1b and 2b show the band scheme of the heterojunction at equilibrium and during UV irradiation. Considerations similar to those made for the Si/n-InP case can be applied to this system at equilibrium (fig. 1b).

As like as in the previous system, when photons impinge on the sample, electrons jump in the conduction band; the holes left in the valence band still can go towards the Si layer both by tunneling effect (path b, fig. 2b) and by thermionic effect (path c). The photocurrent, instead, is made of the holes driven away from the junction by the bulk potential (path a). The electrons driven to the junction region by the bulk potential remain there trapped by the conduction band "notch". At room temperature they can recombine with holes through interface states or can jump on the

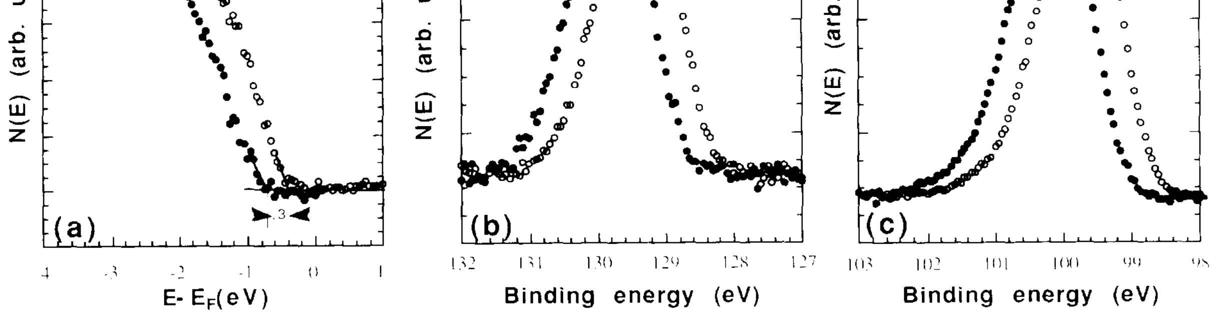

Fig. 3. Valence band (a), P 2p (b) and Si 2p (c) spectra of Si/n-InP heterojunction obtained at room temperature (RT) – open circles – and at 120 K (LT) – full circles –. At low temperature there is a rigid shift of 0.3 eV to higher binding energies of all the spectral features.

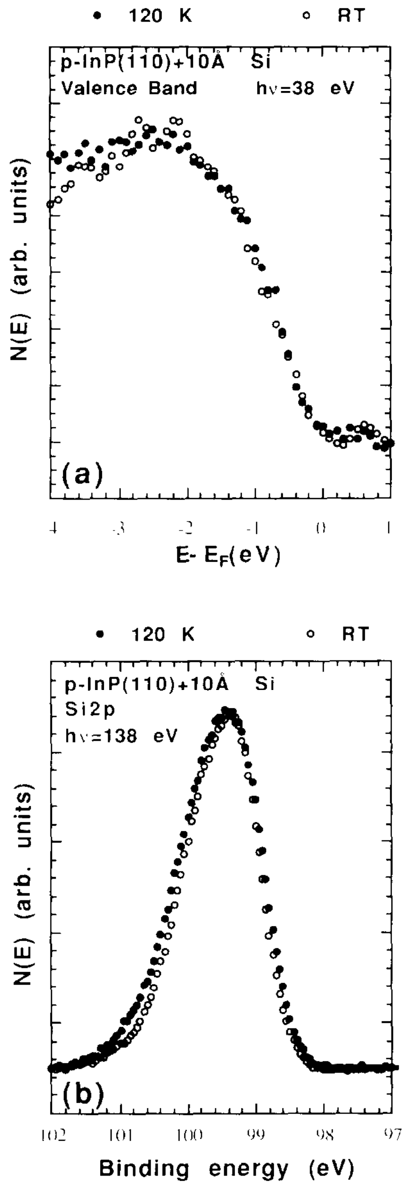

Fig. 4. Valence band (a) and Si2p (b) photoemission spectra of Si/p-InP heterojunction taken at RT – open circles – and LT – full circles –.

Si side by thermionic effect (path c′, fig. 2b). The behavior of the heterojunction Si/p-InP is therefore the same of the previous system at room temperature. Restoring effects (thermionic current, tunneling current and recombination) balance the photoinduced current and the bands structures remain unchanged. As previously said, the restoring effects are lowered at low temperature; in this situation we should obtain a separation of positive and negative charges at the two sides of the junction, and we should find an interface electrostatic dipole. The creation of such a dipole should shift to opposite directions the spectral features coming from the Si overlayer and from the InP(p) bulk. This implies a change of the band discontinuity of this heterojunction only due to the SPV effect. Despite of these considerations our spectra do not show the presence of any dipole, nor band discontinuity changes. The absence of the predicted effect can be explained by assuming that there is a more efficient recombination mechanism for this interface, or we did not lower enough the temperature to reduce the restoring current. We noticed that in ref. [22] a surface-recombination velocity study at InP-metal interfaces has shown that the electron–hole recombination time is strongly dependent on interface states density, being higher for states closer to midgap. We cannot exclude that, also in our case, empty midgap states at Si/p-InP interface play a major role in the restoring current.

4. Conclusions

We have proved that a SPV effect can be easily observed in staggered gaps heterojunctions and that, also in these systems, due to bands flattening, the valence band discontinuity can be directly measured by core levels photoemission studies at low temperature. We did not succeed in photoinducing an electrostatic dipole at the interface due to the extremely high electron–hole recombination current even at low temperature. It seems quite important a better control of the overlayer growth to reduce the interface states density and the recombination current.

There are some attempts to get some insight into the problem of the dipole formation. The first and the most trivial one is to lower the temperature to 100 K or less. We expect that at lower temperature the recombination processes could be decreased and the dipole could be created. Experiments on CdTe/n-GaAs by Xiaohua Yu et al. [21] were performed at temperature as low as 30 K, where they found a complete flat band condition. Furthermore the efficiency of the surface photovoltage depends on the concentration of dopants [16]. A more systematic study of the SPV effect for heterojunctions as a function of this parameter is required.

A further attempt to increase the understanding of this phenomenon may consist in separating the photoemission process from the formation of the electron–holes pairs, by using two different light sources. For instance a low energy light source may be used to stimulate the excitation of the electrons and synchrotron radiation may be used for core levels analysis.

A different tool to determine the position of the Fermi level of the system without creating electron–hole pairs (other than the ones due to the low energy light source) may be a Kelvin probe.

Acknowledgement

This research was supported by the Italian CNR and the University of Wisconsin.

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