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Electronic structure at InP organic polymer layer interfaces

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Organic polymer layer/p-InP(100) interfaces have been investigated using surface photovoltage spectroscopy (SPS) in conjunction with ultraviolet-visible absorption spectroscopy (AS), infrared transmission spectroscopy (IRTS), time-resolved photoluminescence (PL), and x-ray photoemission spectroscopy (XPS). Prior to deposition, the etched p-InP(100) surfaces exhibited two gap states, attributed to excess surface P and adsorbed O, respectively. Postdeposition measurements show that N-containing layers suppress the former state at the interface, while the latter state is suppressed if S and F are present in the organic polymer film. A mechanism of these interfacial phenomena is suggested. © *1997 American Institute of Physics.* [S0003-6951(97)03322-6]

InP-based devices are rapidly becoming dominant in high mobility[1] and optoelectronic[2] device technologies. A wide spectrum of organic layers are used on InP and other semiconductors in different capacities.[3–7] These layers are attractive because they are inexpensive to fabricate, ambient stable, and chemically inert (in contact with inorganic materials). This is especially important in view of the problematic nature of native oxides as dielectrics for III–V based field-effect transistors (FETs). Hence, understanding the properties of such interfaces is of interest.

In this letter, we report on a study of interfacial effects at heterojunctions of organic layers, deposited onto etched p-InP(100) surfaces. The studied layers are specific polymer films, which may serve as potential dielectric layers for InP gates, but not for passivation or as diffusion barriers. The electronic structure at such interfaces is of crucial relevance to the transport properties of the FET's channel.[3] The light absorption, elemental composition, chemical structure, and carrier lifetimes have been studied by absorption spectroscopy (AS), x-ray photoemission spectroscopy (XPS), infrared transmission spectroscopy (IRTS), and time-resolved photoluminescence (PL), respectively. The main objective of this study was to investigate the electronic structure of the heterojunction interfaces using surface photovoltage spectroscopy (SPS)[8] with the aid of the above-mentioned complementary techniques.

The SPS experiment is based on the classical Kelvin probe technique,[9] which measures the work function difference [known as the contact potential difference (CPD)] between a metallic reference probe and a semiconductor surface [Fig. 1(a)]. The semiconductor and reference probe are placed in a capacitor arrangement with the distance between them kept to a fraction of a millimeter [Fig. 1(b)]. Vibration of the metallic probe, induces ac capacitance between the probe and the semiconductor, which results in an ac current in the external circuit. The ac current value is zero, if and only if, there is no charge on the capacitor. In this case, there can be no electric field between the probe and sample, i.e., the CPD must be zero. Hence, an external compensating dc bias, which aligns the probe and sample vacuum levels and

results in a zero ac current, is equal and opposite to the CPD. Both the space charge and the surface charge may change very significantly under illumination. The absorbed photons can modify the charge distribution within the semiconductor since they produce free carriers by photoinduced charge exchange between the valence band, gap traps, and the conduction band. Thus, a significant amount of charge may be redistributed within the surface and/or the bulk.[10] Since the electric potential depends on the charge distribution via the Poisson equation, the surface potential may change, i.e., a surface photovoltage (SPV) may develop. The dashed lines in Fig. 1(a), represent the flattened bands due to light-induced surface charge separation in p-type semiconductor. Under such conditions, the surface work function increases. One can also observe that a change in the CPD may result from a change in the effective surface electron affinity, i.e., the CPD may change keeping the semiconductor bands unaffected with respect to the Fermi level. However, such a change is possible only through a photochemical response, altering the surface electron affinity by modifying the surface dipole contribution.[11] Thus, in the absence of photochemical activity, changes in the CPD are equal to changes in the surface band bending. A change in carrier quasi-Fermi level upon illumination is, by itself, not a sufficient condition for producing a CPD change. Only if the position of the semi-
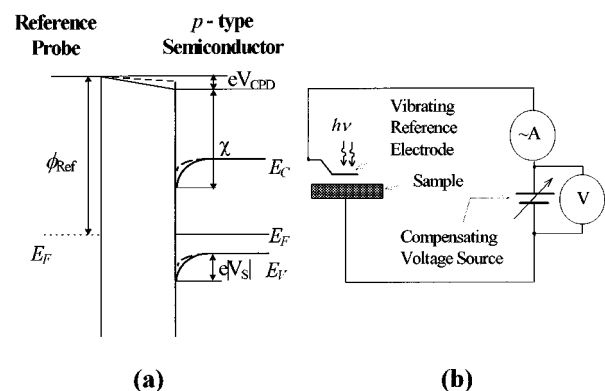

FIG. 1. (a) Energy band diagram of a p-type semiconductor in equilibrium (solid lines) and under illumination (dashed lines). (b) Schematic diagram for CPD evaluation circuit.

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TABLE I. The source gas mixtures used in the PECVD of the organic polymer layers and their resulting elemental composition.

| No. of sample	Discharge gas mixture	Elements in film as observed by XPS
1	Ar,He,C_2H_2	C,O
2	Ar,He,C_2H_2,O_2	C,O
3	Ar,He,C_2H_2,N_2	C,N,O
4	Ar,He,Si$(CH_3)_4$,N_2	C,Si,N,O
5	Ar,He,C_2H_2,SF_6	C,F,S
6	Ar,He,Si$(CH_3)_4$,SF_6	C,Si,F,S
7	Ar,He,Si$(CH_3)_4$	C,Si,O
8	Ar,He,Si$(CH_3)_4$,O_2	C,Si,O

FIG. 2. Typical SPV spectrum of the substrates after etch and before deposition. Inset: suggested InP surface band diagram deduced from the spectrum.

conductor vacuum level at its surface varies with respect to the Fermi level of the metallic probe (or, equivalently, that of the semiconductor's back contact) will a CPD change occur. Carrier generation per se is also not a sufficient condition for the formation of SPV (CPD change), since it does not change the net charge at the point of generation. SPV develops only if the charge generation is accompanied by net charge separation.

The substrates used were (100) oriented Zn-doped (5.7×10^{16} cm^{-3}) p-InP wafers supplied by Crismatec (InPact) France. Each sample was etched by a 1:1:2 HCl(36.46%):HNO$_3$(65%):H$_2$O (doubly distilled) solution for 20 s, rinsed in doubly distilled water and dried in air ambient. Organic polymer layers were deposited by plasma enhanced chemical vapor deposition (PECVD)[12] onto the samples. Table I shows the source gases of the different films deposited. The chemical structure and elemental composition of the layers were analyzed using XPS and IRTS. The right-hand side column in Table I shows the elements as detected by XPS after initial sputtering of the organic polymer layers on the samples. AS measurements determined the light transmission of the films in the ultraviolet-visible region.[12] The carrier lifetimes of the different samples were characterized using PL.[13] The surface electronic structure of all the samples was investigated by SPS. In the SPS system, the surface photovoltage (SPV)[8] was monitored using a commercial Kelvin probe unit with ~ 1 mV sensitivity. The sample under investigation, was illuminated from the organic polymer layer side by light from a 250 W tungsten–halogen lamp that passed through a 0.25 m grating monochromator. The output illumination power at the sample surface typically lies in the μW region.

Figure 2 shows a typical SPV spectrum of the substrates after initial etch and before deposition (the suggested InP surface band diagram deduced from the spectrum is given in the inset). The upward slope change at 1.04 eV indicates population of a gap state situated at $E_v + 1.04$ eV (denoted in the inset by D_1), where E_v is the valence band maximum. The upward offset at 1.18 eV is not a state and is caused by changing the optical filter. The downward slope change at 1.2 eV indicates depopulation of a state situated at $E_v + 0.15$ eV (denoted in the inset by A_1). The InP band-to-band transition causes the slope change observed at 1.35 eV,[14] which is upward as expected for p-type materials. The analysis of the surface spectrum (Fig. 2) makes it possible to suggest a schematic band structure diagram of the sample
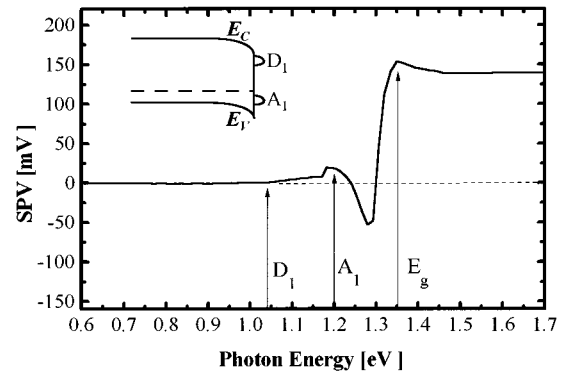
surface (which is shown in the inset of Fig. 2). We attribute the two states—A_1 and D_1, typically exhibited by all the samples prior to deposition, to excess P and adsorbed O at the surface, respectively. Similar assignments were made in the past.[15] Intensity-resolved SPV measurements were made to check whether the states in question were interface states or bulk states. The SPV signal from both states reached a full saturation, i.e., total population/depopulation indicating the existence of two surface gap states, rather than InP bulk states.[10] In a complementary experiment, aggressive etching was performed on the reference substrate.[16] This resulted in a suppression of both states, which gradually recovered over time. Further study of the recovery dynamics reveals that D_1 recovers almost instantly while A_1 recovers during the first 72 h in air ambient but never reaches its original magnitude. It seems that the remaining A_1 is ''masked'' by etch residues which gradually desorb. These findings are in accord with the suggestion that D_1 (A_1) is due to adsorbed O (excess P) at the InP surface.

Figure 3 shows the SPV spectra of the deposited samples. A look at the spectra of the different samples reveals the following phenomena: Samples 1 and 2 yield the same spectrum as the reference substrate (see Fig. 2), samples 3 and 4 show a similar spectrum except that the transition due to the A_1 state is suppressed, samples 5 and 6 yield the same spectrum as the reference substrate but their D_1 transition is suppressed, samples 7 and 8 (not shown)
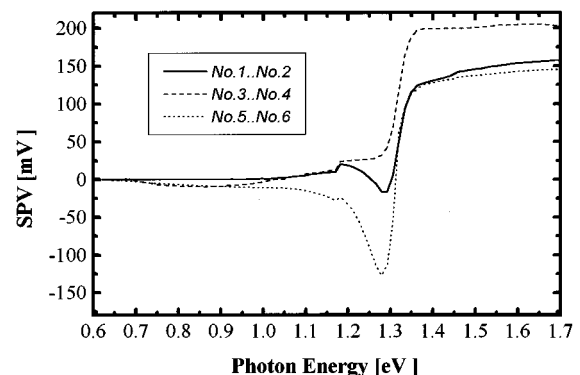

FIG. 3. Typical spectra of the samples coated with the various organic polymer layers.

exhibited the same (but enhanced) characteristics of the reference substrate.

In order to make sure that the SPS data described above are indeed obtained from the organic polymer layer/InP junctions, absorption spectroscopy (AS) measurements were carried out. They showed good light transmission (nearly 90%) of the organic polymer layers in the illumination region corresponding to the SPV measurements, with some increased absorption in the blue region. Thus, light from our monochromator could reach the interface and the SPV could be directly affected by it.

The data of the eight deposited samples reveal two interesting phenomena (Fig. 3): (1) The A_1 surface state is suppressed only by nitrogen-containing films (Nos. 3 and 4). (2) The D_1 surface state is suppressed only by films containing sulfur and fluorine (Nos. 5 and 6). XPS measurements carried out on these samples suggest ion exchange of P by N,[17,18] on the one hand and of O by S (Refs. 19 and 20) and F on the other hand. The presence of C, H, and O in the films does not seem to change the original substrate spectrum (Nos. 1 and 2).

Time-resolved PL measurements yielded a mean lifetime (τ) of the charge carriers near the surface. All the substrates exhibited a uniform carrier lifetime of ~ 0.25 ns (literature values are around 7 ns).[14] This indicates a considerable surface trap concentration. The lifetime did not change after the organic polymer layer deposition. The super-band-gap SPV signal depends on the initial (dark) band bending and the carrier lifetime. Since the carrier lifetime is identical in all samples, one can assume that the super-band-gap SPV signal reflects the ''dark'' (i.e., in equilibrium, not in steady state) interface band bending. Indeed, Fig. 3 shows that samples Nos. 3 and 4 exhibit higher band bending, while samples Nos. 5 and 6 show a somewhat lower band bending relative to the reference substrate. This is consistent with the model of the electronic structure presented above. Samples Nos. 3 and 4 have shown the suppressed excess P induced state (A_1) and a resulting higher net positive interface charge density (see inset in Fig. 2), which dictates a higher band bending, as observed. The opposite trend in a milder form is shown by samples Nos. 5 and 6.

In conclusion, we have characterized the electronic structure of organic polymer layers/InP interfaces using SPS and complementary techniques. Good correlation was found between the presence of particular species in the film and the suppression of the gap states attributed to surface O and excess P, respectively. The organic polymer layer induced changes in the interface chemical composition, probably upon reactions involving free radicals, and the resulting electronic structure may be used for interface engineering of these important heterojunctions and devices based on them.

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