PHYSICAL REVIEW B, VOLUME 64, 235331

Photoemission study of chemisorption of C_{60} on InP(100)

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(Received 1 March 2001; published 28 November 2001)

The growth mode and electronic structure of C_{60} molecules adsorbed on InP(100) were studied by x-ray photoemission spectroscopy and ultraviolet photoemission spectroscopy as a function of coverage and annealing temperature. The C $1s$, P $2p$, In $4d$ core levels and the valence band photoemission spectra point to the presence of a localized covalent bond between the C_{60} molecules and the substrate. No filling of the lowest unoccupied molecular orbit derived bands was observed. The absence of any change in the surface components of the In $4d$ core level upon C_{60} adsorption indicates that the chemisorption bond exists between the fullerene molecules and P atoms rather than between C_{60} molecules and In atoms. This assertion is supported by the simultaneous desorption of both C_{60} and P upon annealing to 640 K and above.

DOI: 10.1103/PhysRevB.64.235331 PACS number(s): 68.43.−h, 73.20.Hb, 79.60.−i, 73.61.Wp

I. INTRODUCTION

The growth of C_{60} films on many kinds of surfaces has become a topic of great interest in recent years.[1] The interaction of C_{60} with semiconductor surfaces, such as Ge,[2] Si,[3–9] and GaAs (Refs. 10–12) has been the subject of intense experimental investigation because of the potential industrial applications of these systems. The interaction of C_{60} with Si is predominantly covalent and strong[3–9] the substrate-adsorbate interactions tend to dominate the weak C_{60}-C_{60} interactions, and the molecules are immobile at room temperature (RT), forming structures with no long-range order.[5,8,9] Moreover, the fullerene molecules do not desorb from the low-index Si surfaces even at 1000 K, while above this temperature they fragment to form a SiC film.[3,4,7,13] Normally, the interaction of fullerenes with GaAs surfaces is so weak that the fullerene-fullerene interaction dominates the observed structure, resulting in the growth of a fcc(111) face. Only in the case of the GaAs (001)-(4×2) As-rich surface, a second "strained" fullerene structure is observed for which an ionic type of bonding has been suggested, stronger than the bond formed with the other GaAs surfaces.[10–12,14] Photoemission studies demonstrated that C_{60} adsorption on GaAs did not affect As $3d$ and Ga $3d$ core levels but let only to a slight change of the width of the C $1s$ level.[12]

With respect to possible applications in devices, the InP(100) surface is also of major interest. To our knowledge, however, no study has been made of the interaction of C_{60} with InP(100). In this paper we investigate the nature of bonding between adsorbed C_{60} and InP by means of photoemission. We present a detailed analysis of the changes in C $1s$, P $2p$, and In $4d$ levels as well as in the valence-band spectra as a function of coverage and annealing. The results reveal evidence of covalent bonding between the fullerene and InP surface, the existence of a preferential chemisorption bond between C_{60} molecules and P atoms rather than between C_{60} molecules and In atoms, and significant desorption of C_{60} coupled with the growth of metallic indium clusters when annealing temperature was increased to 640 K and above.

II. EXPERIMENTAL

The InP(100) samples were cut from polished wafers and were cleaned by a chemical etching treatment.[14] Once prepared, samples were rapidly introduced into an ultrahigh vacuum (UHV) chamber at pressures below 5×10^{-10} Torr. The wafers were n-type InP(100) (S-doped with $n=2\times10,^{17}$ wafer thickness 400 μm; the reported resistivity was $1.5\times10^{-2}\ \Omega$ cm) purchased from Wafer Technology, Ltd. An In-terminated InP (100)-2×4 reconstruction[14–16] was prepared by performing several cycles of sputtering (Ar^+ ions, 0.5 keV beam energy, 1 μA sample current) and annealing, until no impurities could be detected by photoemission, and sharp low-energy electron diffraction (LEED) patterns characteristic of the clean surface were observed.[14,15] Photoemission spectra were acquired with a SCIENTA SES-200 analyzer using Mg$K\alpha$ x rays and a helium-discharge lamp for core-level [x-ray photoelectron spectroscopy (XPS)] and valence-band [ultraviolet photoemission spectroscopy (UPS)] spectra, respectively. The experimental resolution was 0.85 eV (0.09 eV) for XPS (UPS) photoemission spectra. Binding energies for UPS spectra were referenced to the Fermi level of a Ta plate at the base of, and in electrical contact with, the sample holder. XPS binding energies were calibrated using the bulk In $4d$ line employing the binding energy value obtained from the corresponding He II spectrum. C_{60} was deposited from a thoroughly outgassed home-built tantalum cell onto the clean surfaces. Fullerene deposition was carried out with the sample at room temperature (RT). During C_{60} sublimation, the chamber pressure was maintained below 3×10^{-9} Torr. The C_{60}/InP(100) monolayer coverage was defined as the saturation coverage left on the InP surface after annealing a C_{60} multilayer film at 600 K.[17] Other coverages were de-

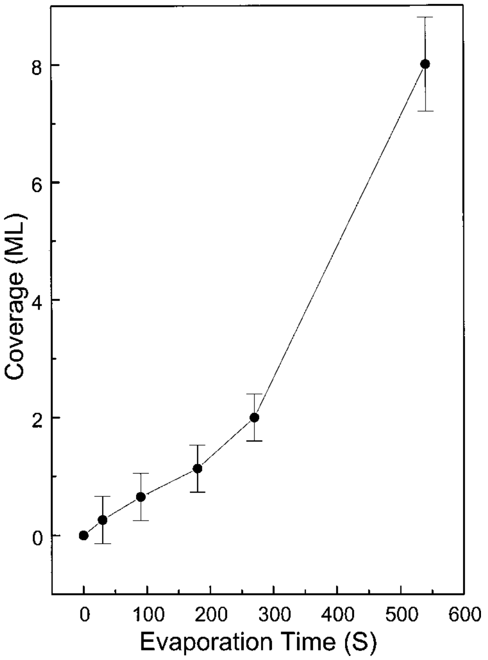

FIG. 1. Fullerene coverage vs exposure time. 1 ML coverage was defined as the saturation coverage left on InP surface after annealing a C_{60} multilayer film at 600 K. Other coverages were deduced from the peak heights of the C1s photoemission line relative to those of the In 3d level.

duced from the peak intensities of the C 1s photoemission line relative to those of the In 3d level.

III. RESULTS AND DISCUSSION

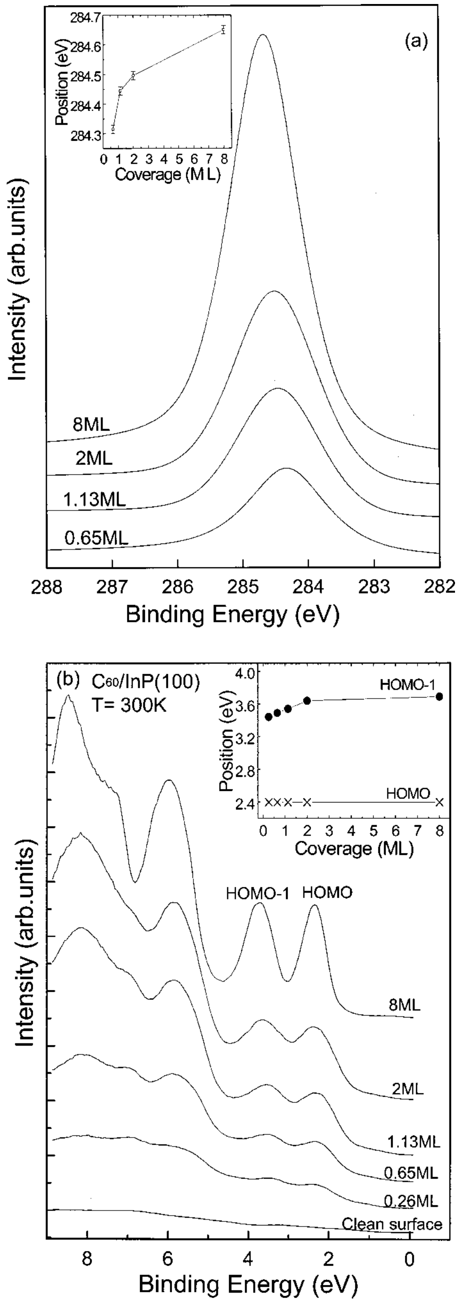

FIG. 2. (a) C 1s photoemission spectra ($h\nu = 1253.6\,\mathrm{eV}$) for 0.65 ML and 1.13, 2, and 8 ML of C_{60} on InP(100). The inset shows the relationship between C 1s peak position and coverage. (b) Valence-band photoemission spectra ($h\nu = 21.2\,\mathrm{eV}$) collected for 0.26, 0.65, 1.13, and 8 ML of C_{60} on InP(100). The inset shows the HOMO and HOMO-1 peak position vs coverage; the error bars are within the size of the dots.

Figure 1 shows the relationship between C_{60} coverage and evaporation time: it exhibits the typical three-dimensional (3D) (Vollmer-Weber) growth mode behavior. The same growth mode has been observed by STM (Ref. 10) for C_{60} on GaAs(110). Further information about the growth mode and C_{60}-InP interaction can be gained from the C 1s photoemission line. Figure 2(a) presents spectra for a range of coverages of C_{60} on InP(100). The insert shows the C 1s peak position vs coverage. With increasing coverage, the C 1s binding energy (E_B) is shifted to higher binding energies. The C 1s binding energy for 0.65 ML is 0.34 eV lower than that for 8 ML, which is located at 284.65 eV. This shift is mainly due to reduced image screening for molecules in the multilayer.[18] In addition, the full width at half maximum (FWHM) of the C 1s line at submonolayer coverages is increased to 1.46 eV in comparison to a FWHM of 1.27 eV at a coverage of 8 ML. An asymmetric line shape is observed even above monolayer coverage resulting from the 3D growth mode at room temperature—molecules in several incomplete layers are probed, the core hole in each layer experiencing a different degree of screening and hence displaying slightly different binding energies.[18] A very small broadening of ~0.1 eV of the C 1s line was reported for C_{60} adsorbed on GaAs.[12] Changes in the electronic structure of C_{60} brought about by adsorption can be further assessed by comparing valence-band spectra of 1.13 ML C_{60}/InP(100) with those of submonolayer (0.26 ML, 0.65 ML) and multilayer (2 ML, 8 ML) films on the same substrate, as shown in Fig. 2(b). Comparing submonolayer with multilayer spectra, we notice that the position of the highest occupied molecular orbital (HOMO) stays constant, while the HOMO-1 shifts to higher binding energies. This nonrigid band shift is a signature of chemical bond formation, in particular hybridisation, between the substrate and adsorbed fullerene molecules, although it is usually accompanied by significant extra broadening[17,19] of the HOMO-1 related feature, absent in this case.

To determine more about the nature of the substrate-adsorbate bond we recorded P $2p$ core level XPS spectra and In $4d$ UPS spectra with different C_{60} coverages. Figure 3(a) shows P $2p$ core levels for a range of coverages of C_{60} on InP(100). The inset shows the P $2p$ peak of clean InP, and with C_{60} coverages of 0.65 and 8 ML, all normalized to the same peak height after subtraction of the background. It is clear from the inset that there is a small shift in line position and corresponding change in line shape with C_{60} coverage, which can be associated with a shift of a surface-related component of the P $2p$ line. The three-dimensional growth results in changes to the P $2p$ line shape even above a nominal 1 ML coverage. Figure 3(b) shows the line shape analysis of the P $2p$ core level photoemission spectrum of 2 ML C_{60} on InP(100); this was fitted two mixed doublets and a Shirley background. During the fitting procedure the spin-orbit splitting was kept fixed at 0.86 eV and the branching ratio set to 0.5.[20] The inset shows surface component peak position vs coverage. With increasing coverage, the P $2p$ surface component peak position shifts to higher binding energies. This is indicative of a chemisorption bond between C_{60} molecules and P atoms.

For In $4d$ UPS ($h\nu = 40.8\,\mathrm{eV}$) spectra, the line was fitted with three mixed doublets and a Shirley background. Surface component (3) is attributed to the In-P bond,[14–16,20] while the surface component (2) is still not uniquely assigned.[14,15] During the fitting procedure, spin-orbit splitting was kept fixed at 0.86 eV; the branching ratios were 0.65.[20] Figure 4(a) shows the line shape analysis of the In $4d$ photoemission spectrum ($h\nu = 40.8\,\mathrm{eV}$) of 0.26 ML C_{60} on InP(100). The inset of Fig. 4(a) shows the binding energy of the surface component (3) of the In $4d$ line as a function of C_{60} coverage. It is clear that there is no change in binding energy over the coverage range studied nor after annealing (open circle). The same observation is made for the surface component (2). This implies that there is no significant perturbation of the surface In atoms by the adsorbed C_{60} and that consequently bonding is localized between the adsorbed C_{60} and the surface P atoms.

The localization of chemical bonding between the C_{60} and P is indicative of a primarily covalent interaction between the adsorbed C_{60} and the InP(100) surface—charge transfer interactions are generally delocalized and would be expected to perturb *both* the In and P core lines contrary to our observations. The absence of appreciable charge transfer is reflected in the valence band spectra of Fig. 5(b). Any transferred charge would have to be accommodated in the normally empty t_{1u} lowest unoccupied molecular orbital which can result in the presence of fullerene-related photoemission features near the Fermi level (E_F).[21,22] Such features are noticeably absent from our valence band spectra at all C_{60} coverages and under all annealing conditions used.

To follow changes in the adsorbed C_{60} layers upon annealing, we recorded C $1s$ XPS after annealing at 600, 640, 690, and 740 K. The results are shown in Fig. 5(a), together with a spectrum from RT-grown 1.13 ML C_{60}/InP(100). Annealing to 640 K causes the core line to shift by 0.1 eV to lower binding energy, and further, a small narrowing of the C $1s$ line is observed. After annealing cycles at 600 and 640 K, the ratio of C $1s$ to In $3d$ peak height is found to be unchanged, indicating that desorption of less strongly bound molecules cannot account for the narrowing of the C $1s$ line.

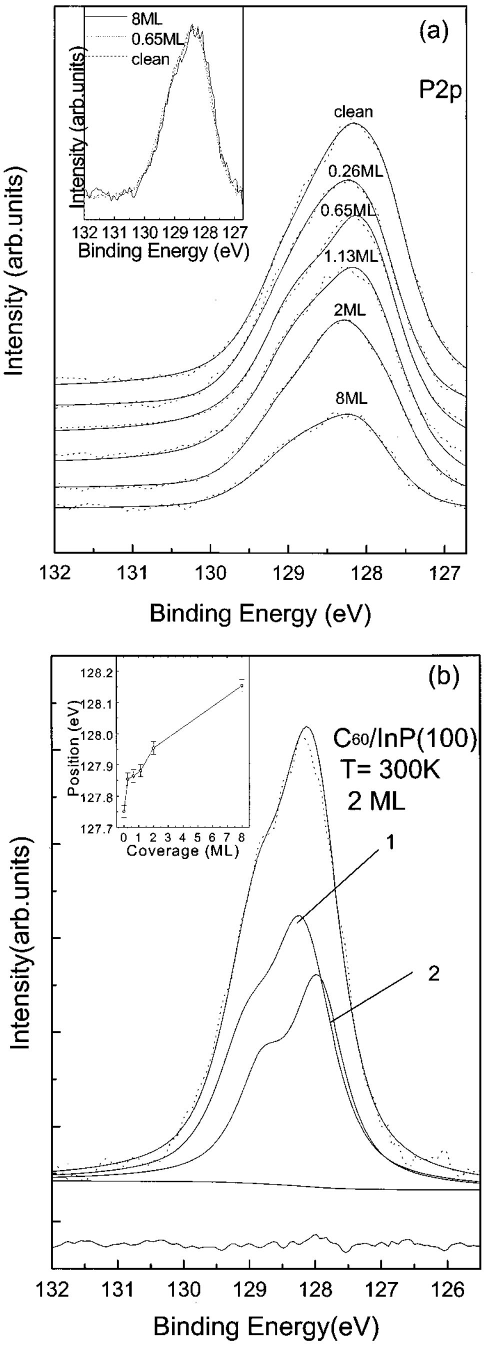

FIG. 3. (a) P $2p$ core level photoemission spectra ($h\nu = 1253.6\,\mathrm{eV}$) of C_{60} on InP(100). The inset shows rescaled spectra of clean InP, and with C_{60} coverages of 0.65 and 8 ML with backgrounds subtracted. (b) The P $2p$ core level photoemission spectrum ($h\nu = 1253.6\,\mathrm{eV}$) of 2 ML C_{60} on InP(100). Experimental spectrum (dotted line) was fitted to a Shirley background and two mixed doublet components: bulk (1) and surface (2) components. The inset shows the surface component peak position vs coverage.

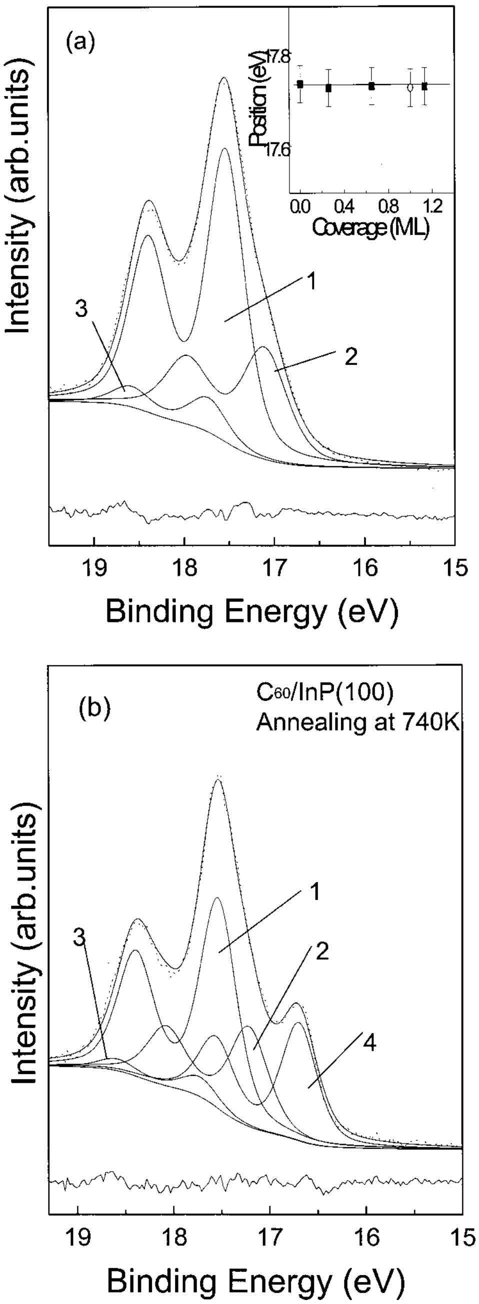

FIG. 4. (a) The In 4*d* photoemission spectrum ($h\nu = 40.8$ eV) of 0.26 ML C_{60} on InP(100). The experimental spectrum (dotted line) was fitted to a Shirley background and three mixed doublet components: bulk (1) and surface (2 and 3) components. The inset shows the indium surface (3) component peak position vs coverage (■), in comparison with that of 1 ML of C_{60} on InP(100) after annealing at 600 K (○). (b) The In 4*d* photoemission spectrum ($h\nu = 40.8$ eV) after annealing to 740 K. The experimental spectrum (dotted line) was fitted to a Shirley background and four mixed doublet components: bulk (1), surface (2 and 3), and metallic indium (4) components.

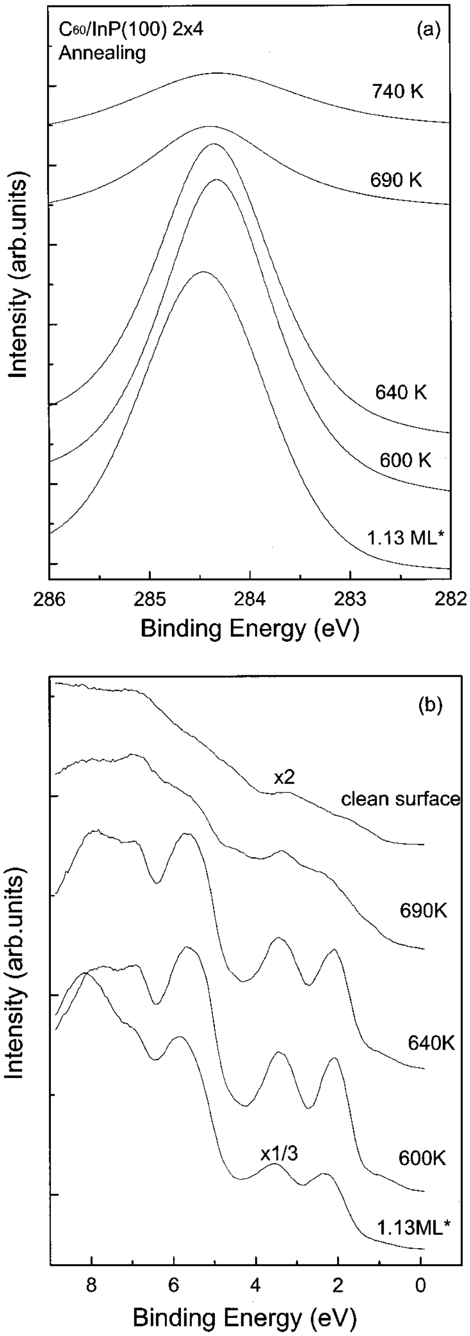

FIG. 5. (a) C1*s* photoemission spectra ($h\nu = 1253.6$ eV) of C_{60} on InP as deposited at RT and after various annealing steps. Also plotted, for comparison, is the C 1*s* spectrum of 1.13 ML C_{60}/InP (100) before annealing. (b) Valence-band spectra ($h\nu = 21.2$ eV) collected for C_{60} on InP(100) as deposited at RT and after various annealing steps. Spectra from the clean surface and a coverage of 1.13 ML C_{60}/InP (100) before annealing are plotted for comparison.

Therefore, the narrowing probably arises from changes in adsorption state and or better ordering of the fullerene molecules in the film. These changes are reflected in the valence band UPS spectra from the same surfaces. The results are shown in Fig. 5(b), together with a spectrum from RT-grown 1.13 ML C_{60}/InP(100) and a spectrum from the clean InP(100) surface. Annealing to 640 K causes HOMO peak position shift by 0.3 eV and HOMO-1 shift by 0.1 eV towards higher binding energy. After annealing to 690 K, substantial desorption of carbon is observed and the ratio of

C 1s to In-3d peak height is reduced by about one third. Further broadening of the valence band features is observed at this temperature with the fullerene-related signal superimposed on a strong background from the InP surface.

It is found that, with increasing annealing temperature to 640 K, there a small metallic component in the In 4d core level photoemission spectrum appears, which indicates the presence of metallic indium clusters. Previous work on sputtering of InP (Ref. 23) shows a similar component which arises due to the preferential sputtering of phosphorous. Thus, the metallic indium component is a characteristic signature of phosphorous desorption from the InP(100) surface. The intensity of metallic indium component rises with increasing temperature, while intensity of both C 1s and P 2p peaks falls. This indicates that C_{60} and phosphorous might desorb together from the surface and thus this could be a further support for the conclusion that bonding between C_{60} and InP(100) is mediated by covalent bonding with surface P atoms, the surface In atoms playing a passive role. Figure 4(b) shows the In 4d photoemission spectrum ($h\nu = 40.8$ eV) after annealing to 740 K. The experimental spectrum (dotted line) was fitted to Shirley background and four doublet components: bulk (1), 2 surface (2,3), and metallic indium (4) components. The metallic In component is clearly visible and is at a different binding energy to the surface component (2), enabling a clear differentiation between the two In species.[16]

In the literature there is still considerable debate about reconstruction models for the In rich (2×4)InP(100) surface, since it has been found that there is no direct analogy to GaAs(100) (Ref. 15, and references therein). It has recently been suggested on the basis of STM studies,[24,25] total energy calculations,[27,28] and angle resolved photoemission spectroscopy[15,28] that simple In-In dimers or trimers are not solely present on this surface, but that there is evidence that there is also a considerable fraction of mixed In-P dimers[15,24,25,27,28] or even P-P dimers[25,26] present. Our results are in agreement with these findings—the presence of P at the outermost surface is necessary for C_{60} to bond to the phosphorous. Normally, isolated P behaves as an electron donor and C_{60} as an acceptor. If a P-P dimer is formed on the InP(100) surface a dangling p orbital is present, or for the case of the In-P mixed dimer a σ-like bond is formed by in plane In sp^2 hybrids and a P p orbital.[28] Since we did not observe any significant changes in the In 4d surface components within our resolution, there is a strong possibility that P-P dimers are present on the InP(100)-(2×4) surface. However, it is also possible (although unlikely given the lack of change in the surface components of the In 4d line) that the adsorption of C_{60} may lead to a new surface reconstruction which involves the presence of surface phosphorous dimers. Further experimental investigations are necessary to fully resolve this issue.

IV. CONCLUSIONS

In conclusion, we have found that C_{60} molecules adsorbed on InP(100) at room temperature form a chemical bond with the substrate, but without any observable charge transfer into the lowest unoccupied molecular orbital (LUMO) of the C_{60} molecule from the substrate. The resulting covalent bonds are localized between the C_{60} molecules and surface phosphorus atoms. This assertion is supported by evidence from annealing experiments which show simultaneous desorption of carbon and phosphorous. Careful analysis of In 4d core level spectra indicate that there is no detectable interaction between the C_{60} and surface In atoms, suggesting the presence of P-P or mixed In-P dimers in the surface reconstruction of the substrate.

ACKNOWLEDGMENTS

Y. C. is grateful to the scholarship panel of Newcastle University for award of a Development Trust Bursary. L. Š. is grateful to EPSRC and Royal Society for financial support. We thank Mr. G. Miller for valuable technical support. We are grateful to Professor Y. Fukuda for providing detailed information on cleaning InP.

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