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LETTER TO THE EDITOR

Surface passivation of (100) InP by organic thiols and polyimide as characterized by steady-state photoluminescence

M Schvartzman[1], V Sidorov[2], D Ritter[2] and Y Paz[1,3]

[1] Department of Chemical Engineering, Technion, Haifa 32000, Israel
[2] Department of Electrical Engineering, Technion, Haifa 32000, Israel

E-mail: paz@tx.technion.ac.il

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Abstract
A method for the passivation of indium phosphide, based on thiolated organic self-assembled monolayers (SAMs) that form highly ordered, close-packed structures on the semiconductor surface, is presented. It is shown that the intensity of steady-state photoluminescence (PL) of n-type InP wafers covered with the thiolated SAMs increases significantly (as much as 14-fold) upon their covering with the monolayers. The ease with which one can tailor the outer functional groups of the SAMs provides a way to connect this new class of passivators with standard encapsulators, such as polyimide. Indeed, the PL intensity of SAM-coated InP wafers was not altered upon their overcoating with polyimide, despite the high curing temperature of the polymer (200 °C).

The tendency of InP to reconstruct its surface [1] and to be oxidized [2] is known to produce a high density of surface states within the bandgap and rigid pinning of the Fermi level [3]. As a consequence, the performance of InP-based microelectronic devices is severely damaged. One of the means to improve the performance of microelectronic devices is to passivate their surfaces. Passivation of III–V surfaces is often done by treating the surface with inorganic sulfur compounds [3, 4] such as $Na_2S \cdot 9H_2O$ or $(NH_4)_2S$. Experimental results were theoretically explained [5, 6] on the basis of formation of covalent bonds between the surface atoms and sulfur having energy states outside the fundamental bandgap. A major obstacle in the implementation of sulfur passivation in practical devices is its lack of stability [7]. To overcome this problem, an overcoating made of As_2S_3 or SiN_x is often used [8, 9].

An alternative approach to the use of inorganic sulfur compounds was suggested by Allara *et al* [10, 11], who proposed the use of long-chain organo-sulfur self-assembled monolayers (SAMs) for passivation of GaAs. Here, the characterization of the passivation properties of the SAMs was performed by measuring changes in the Schottky barrier height of a metal/n-GaAs contact due to modification of the semiconductor surface by the monolayer. Further characterization of passivation properties was performed by measuring the increase in the photoluminescence (PL) of GaAs upon coating [12, 13]. The preparation procedure used for GaAs was successfully adapted for the formation of thiolated SAMs on InP(100) [14]. A covalent bonding between the sulfur atoms of the thiolated molecules and the indium atoms on the surface was found by angle-resolved XPS measurements [15].

In this letter, steady-state PL study on the passivation of InP(100) by various thiolated SAMs is presented. It is shown that coating the semiconductor surface with these monolayers significantly increases PL signals, indicating a significant passivation effect. This passivation effect is not altered upon overcoating with polyimide and curing at elevated temperatures.

[3] Corresponding author.

InP wafers ((100), n type, sulfur doped, 10^{18} cm^{-3}) were coated with various thiolated SAMs by a method similar to that of Gu and Waldeck [16]. The procedure consisted of pre-cleaning by ultra-sonication with organic solvents (acetone, methanol and isopropanol consecutively), followed by plasma-ashing with oxygen for 10 min. Then, the wafers were etched in a concentrated (49%) HF solution for 5 min, and immediately rinsed, first with de-ionized water, then with isopropanol, to remove residual water. Subsequently, the wafers were immersed in the alkanethiol-containing solution (0.1 M in VLSI grade isopropanol). During the whole procedure, which lasted 12–30 h, the temperature of the solution was kept at 65 °C. Care was taken to constantly purge the solution with pure nitrogen. The wafers were then removed from the coating solution and rinsed several times with hot isopropanol. Four types of SAM were prepared using the above-mentioned procedure: (a) octadecylthiol (ODT, $CH_3(CH_2)_{17}SH$); (b) mercapto-hexadecanoic acid (MHDA, $HOOC(CH_2)_{15}SH$); (c) mercapto-undecanoic acid (MUDA, $HOOC(CH_2)_{10}SH$) AND (d) mercapto-undecanol (MUD, $HO(CH_2)_{10}SH$).

The SAMs were characterized by XPS. A comparison between the deconvoluted In 3d peaks in the spectra of bare InP and the deconvoluted In 3d peaks in the spectra of coated InP samples confirmed that the thiol groups bind to the indium atoms, as was claimed before [15]. The average thickness values of the SAMs, based on these measurements, were found to be similar to those reported by Gu *et al* [14] and by Yamamoto *et al* [15], within 10%. Another indication for the quality of the SAMs was obtained by FTIR, where the absorbance of the CH_2(a) in ODT, for example, was found to be 3×10^{-3} OD, a typical value for SAMs of such length [10]. The modification of the surface properties upon coating was demonstrated by wettability measurements with water, made with a Kernco instruments goniometer, where advancing contact angles of 60°, 20° and 105° were measured for bare InP, MHDA-coated InP and ODT-coated InP, respectively. Complementary Auger spectroscopy of bare InP and of ODT-coated InP, performed three days after the preparation of the ODT monolayers, revealed that the atomic concentration of oxygen in the latter was significantly lower than in the former (4% versus 25%) due to the HF etching prior to immersion. In parallel, oxidized phosphor that could be noticed in the bare InP could not be found in the thiolated samples. This suggests that a monolayer of ODT is sufficient to prevent oxygen penetration, at least for three days.

The room-temperature steady-state PL spectra of coated and non-coated InP wafers were obtained by exciting the semiconductor with 632.8 nm He–Ne laser light, directing the luminescence signals through a Digikrom 240 monochromator, and measuring them with a Ge detector (EO-817L, NC Scientific Corp.). To minimize the effect of wafer to wafer inhomogeneity on the experimental results, care was taken to perform comparative measurements only with cleaved pieces of the same wafer.

Polyimide is known as a good encapsulator for III–V devices [17]. Hence, some of the PL experiments were performed with polyimide-coated wafers (covered and non-covered with SAM underlayers). The polyimide layers (0.5–0.7 μm in thickness) were applied by spin-on coating

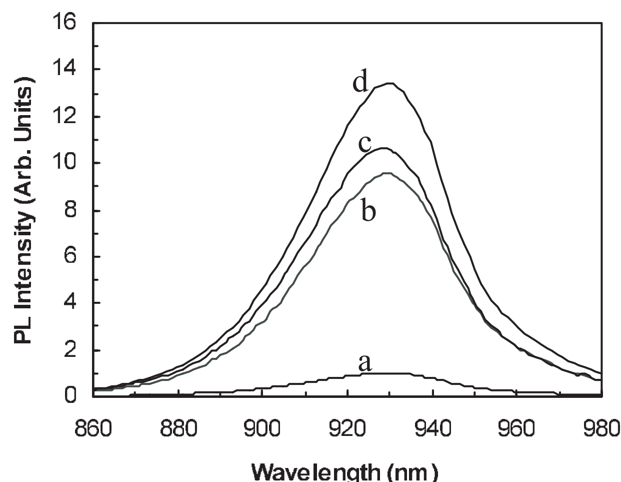


Figure 1. The PL spectra of indium phosphide wafers: (*a*) untreated wafer; (*b*) coated with ODT, immersion time 17 h; (*c*) coated with ODT, immersion time 24 h; (*d*) coated with ODT, immersion time 30 h.

(5000 rpm, 1 min) using a 1 : 1 (v/v) solution of Pyralin™ 2555 (DuPont) and commercial thinner. Curing of the polyimide layer was performed by rapid heating from an ambient temperature to 125 °C, followed by ramping the temperature to 200 °C at 3 °C min^{-1}, dwelling there for 10 min and cooling it slowly to room temperature. In order to remove natural oxide, bare wafers were etched with HF prior to coating with the Pyralin™ solution.

Figure 1 presents the PL spectra for an untreated wafer of indium phosphide and for three other wafers that were coated with an ODT monolayer. An increase in the intensity of the PL signal upon coating, by a factor of 10-14, is clearly observed. This increase was found to be related to the quality of the coating, as can be inferred from the effect of the immersion time in the ODT solution on the PL signal.

It is important to clarify that enhanced PL, as a method for characterizing electrical passivation (i.e. a reduction in the density of surface states), depends heavily on the thickness of the light emitting layer. The shorter this layer is, the more pronounced the effect of surface states is, hence there is expected to be a larger difference in the PL intensity of a passivated semiconductor in comparison with a non-passivated one. For example, passivation of a GaAs wafer with an aqueous solution of Na_2S, a common passivator, increased the PL intensity by a factor of 1.5 with respect to bare wafers [18], while the same passivator increased the PL intensity of a 1 μm epilayer by a factor of 270 [13]. Hence, the 14-fold increase in the PL intensity of InP wafers due to their coating with the ODT monolayer represents a significant passivation effect.

In order to find out whether the increase in the PL signal was due to depletion of oxygen from the surface of the semiconductor, or due to surface passivation by the thiol groups, a comparative study was performed, where the PL intensity of fresh HF-treated InP wafers was compared with that of bare wafers and with that of wafers covered with different thiolated monolayers (figure 2). Unlike the bare HF-treated wafers that were measured immediately after etching, the PL signals of the monolayer-covered wafers were measured a few days after the completion of the coating procedure. The

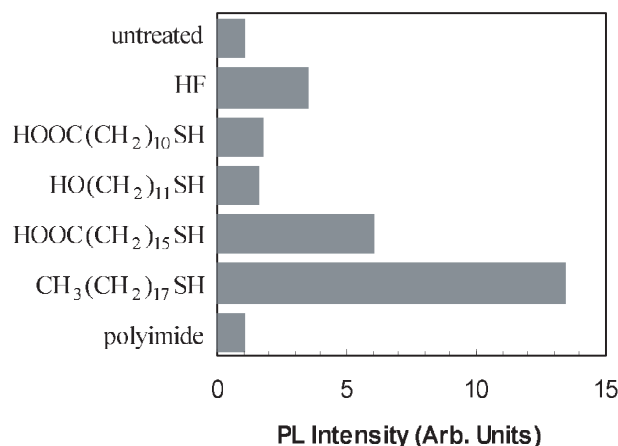


Figure 2. The PL intensity at 928 nm of indium phosphide wafers following various treatments.

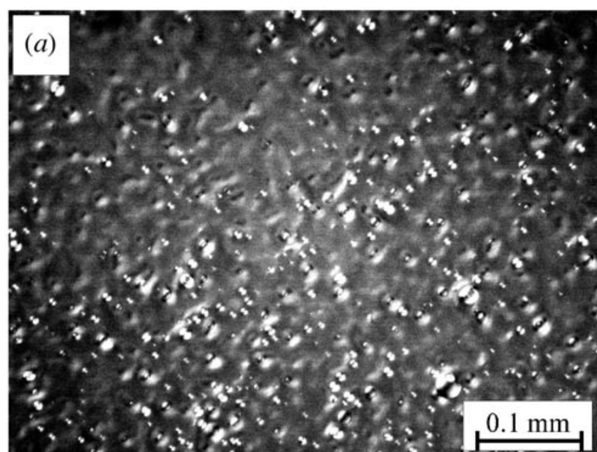
Table 1. The advancing contact angles on ODT-coated InP and on MHDA-coated InP of a commercial polyimide solution (Pyralin^{TM}), its thinner, and a Pyralin^{TM}–thinner (1 : 1 v/v) solution used for planarization.

	Pyralin^{TM}	Pyralin^{TM}–thinner (1 : 1 v/v)	Thinner
Bare InP	$38° \pm 2$	$30° \pm 2$	$25° \pm 2$
InP + ODT	$55° \pm 2$	$59° \pm 2$	$62° \pm 2$
InP + MHDA	$26° \pm 2$	$26° \pm 2$	$17° \pm 2$

PL signals of InP wafers that were etched and immediately coated with 0.6 μm Pyralin^{TM} were measured also a few days after the completion of the procedure. As shown in figure 2, the PL intensity of InP wafers covered with short chains (shorter than 12 carbons) was only slightly higher than that of bare wafers, unlike that of wafers covered with the long alkylthiols. This fact correlates well with the notion that alkylthiol monolayers having short chains are less ordered and less stable [19], hence more prone to oxygen penetration. Apparently, the outer functional groups of the monolayers used for this study have, at most, only a minor effect on the PL intensity. This suggests that the above-mentioned outer groups do not affect the average density of the monolayers and do not play an important role (directly or indirectly) in preventing the penetration of oxygen.

As presented in figure 2, wafers that were coated with a relatively thick layer of polyimide were found to give a very weak PL signal, despite the fact that the coating was performed immediately after the removal of the oxide layer by immersion in hydrofluoric acid. Evidently, the polymer does not form covalent bonds with the InP dangling bonds and hence cannot serve to reduce surface states. Furthermore, it cannot prevent HF-treated InP wafers from losing the beneficial effect of HF treatment.

In order to examine possible compatibility between passivation with organo-thiolated monolayers and existing encapsulating processes, the standard polyimide coating procedure was applied on the thiol-passivated InP wafers. Such compatibility, which is of great importance for standard III–V technology, where horizontal cavities are often formed due to undercuts, depends to a large extent on the wetting of the surfaces by the overcoating solution. The advancing contact angles on ODT-covered InP and on MHDA-covered InP of a commercial polyimide solution (Pyralin^{TM}), its thinner, and a Pyralin^{TM}–thinner (1 : 1 v/v) solution used for planarization are presented in table 1. The table clearly demonstrates the feasibility of using SAMs having hydrophilic outer groups (such as MHDA) to obtain adequate wetting properties. Optical microscopy observations confirmed that polyimide forms a better quality overlayer on MHDA-covered InP than on ODT-covered InP, where bubbles and non-adhered regions could be observed (figure 3).



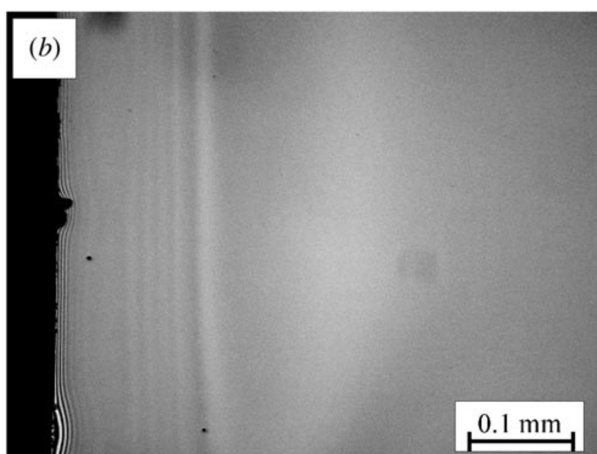


Figure 3. Optical microscopy images of a spin-coated layer of a commercial polyimide encapsulator (pyralin^{TM}) on (*a*) ODT-coated InP wafer and (*b*) MHDA-coated InP wafer.

Figure 4 presents the PL signal of an MHDA-covered InP wafer prior to its overcoating with the polyimide layer and following a 200 °C curing of the polymer. For comparison, the PL spectrum of a bare wafer is presented as well. The PL signal of both the MHDA-covered wafer and the MHDA/polyimide-coated and cured wafer were found to be five times higher than that of the bare InP wafer.

It is well known that non-covered, air-exposed, thiolated SAMs on gold are destroyed at temperatures below 200 °C. The same was found by us in the case of SAMs on InP. Taking into account the fact that polyimide, by itself, does not contribute to passivation (see figure 2), it is noteworthy that the high-temperature curing of the MHDA/polyimide-coated wafer did

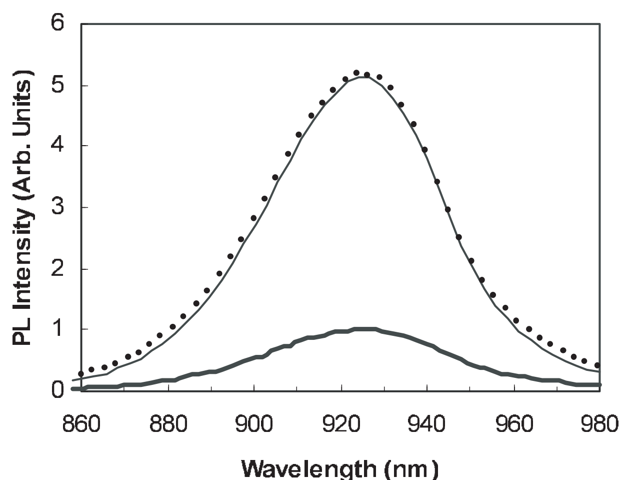


Figure 4. A comparison between the PL spectrum of a bare InP wafer (thick curve) and that of an MHDA-coated InP wafer with (thin curve) and without (dotted curve) a cured polyimide overcoating.

not have any detrimental effect on the PL intensity of the wafer. Apparently, the polyimide overlayer serves as a protective layer for the underlying SAM.

The significance of this letter lies in the fact that it demonstrates the feasibility of using an ultrathin organic layer for the dual purpose of electrical passivation of the semiconductor surface and adhesion promotion of a relatively thick encapsulating layer of polyimide. This connection between this new passivation technique and a standard encapsulating technique may have large prospects in the future.

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