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Citation: *J. Vac. Sci. Technol. B* 21, 148 (2003); doi: 10.1116/1.1532026

View online: <http://dx.doi.org/10.1116/1.1532026>

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Passivation of InP surfaces of electronic devices by organothiolated self-assembled monolayers

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(Received 30 July 2002; accepted 28 October 2002; published 7 January 2003)

Surface passivation with organothiolated self-assembled monolayers (SAMs) that form chemical bonds with the InP surface is described. Indium phosphide surfaces coated with thiolated SAMs were characterized by Fourier-transform infrared spectroscopy, contact angle measurements, and Auger spectroscopy. The steady state photoluminescence of InP wafers increased by a factor of 14 as a result of this surface passivation method. A decrease by one to two orders of magnitude in the dark currents of interdigitated metal–semiconductor–metal diodes and *p-i-n* photodiodes was obtained. The option of using SAMs that are well-wetted by standard encapsulators such as polyimides and the thermal stability of the SAMs at the polymer's curing temperatures open the way to achieve high quality passivation and encapsulation, even when the electronic devices contain negative slope sidewalls or undercut cavities. © 2003 American Vacuum Society.

[DOI: 10.1116/1.1532026]

I. INTRODUCTION

Indium phosphide, a key material for optoelectronic devices, is known to have a high density of surface states within its band gap, which causes Fermi level pinning and a high rate of surface recombination.^{1,2} This situation is aggravated by the introduction of additional midgap states due to the tendency of InP to form native oxides at ambient conditions.³ Unlike silicon, where silicon dioxide seems to be the passivator of choice, the best technology to achieve surface passivation is still to be determined.

Various methods for surface passivation of III–V semiconductor devices were proposed, including hydrogen plasma treatment and deposition of dielectric films such as Si₃N₄, SiO₂, and polyimide.^{4–6} Sandroff *et al.*⁷ proposed a chemical treatment by Na₂S·9H₂O, based on chemical bonding between the sulfur atoms and the surface. This was followed by numerous studies utilizing other inorganic sulfur compounds such as (NH₄)₂S.^{8,9} It was claimed that the midgap surface state density in GaAs is significantly reduced by the formation of Ga–S bonds,^{8,10} however, evidence for the formation of As–S bonds and for the presence of elemental sulfur was also documented. An observation that band bending was increasing upon passivation rather than decreasing led others¹¹ to suggest that passivation by sulfur removes excess As, thus producing positively charged midgap double donor states, which inhibit the recombination between holes and midgap states electrons. Although inorganic sulfur treatments can be quite efficient, their benefits prove to be short-lived unless measures are taken to prevent any exposure to ambient air.¹²

The feasibility of using self-assembled monolayers of long-chain organo-sulfur compounds for surface passivation of III–V semiconductors was first demonstrated for GaAs.^{13–15} Lately, this method was successfully adapted also for InP.¹⁶ Using angle resolved XPS, it was claimed that the sulfur binds to indium atoms, but not to phosphorus atoms, and that the alkyl chains are tilted by 44° relative to the surface normal.¹⁷ Although electrochemical measurements suggested that organothiolated monolayers on InP inhibit oxidation, and affect fluorescence decay,¹⁸ evidence for passivation effects of actual electron devices is still quite scarce.

Photoluminescence intensity and decay measurements are a widely used tool for studying electronic surface properties of III–V semiconductors,¹⁹ and hence provide an indication regarding the quality of passivants. Another tool to demonstrate passivation effects is measuring the dark current in interdigitated metal–semiconductor–metal (MSM) photodiodes under negative bias. Indeed, the dark current in GaAs MSM photodiodes reduced significantly upon passivation with silicon nitride.²⁰ Another type of III–V devices that are highly sensitive to surface passivation are *p-i-n* avalanche photodiodes, where a reduced dark current at applied reverse voltage below the avalanche region is a good indication of the quality of passivation.²¹ Here, some complexity is expected due to the fact that in nonplanar epitaxial technology the active surfaces are the sidewalls of the mesas, whose crystallographic indices depend heavily on the etching techniques and on the orientation of the mask.²² This issue is of importance also because it is believed that organothiolated SAMs form chemical bonds only with indium, hence it is expected that the structure, the tilting angle, and the compactness of these monolayers on InP would depend on the indices of the sidewalls.

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Polyimide is often used as an encapsulator for electronic devices made of III–V semiconductors²³ due to its insulating properties and to its ability to block the penetration of oxygen and humidity. Its properties as a passivant are somehow mediocre, and depend heavily on the semiconductor's type. For example, polyimide coating of interdigitated MSM diodes made of InGaAs decreased the dark current, while the same treatment of diodes made of GaAs increased the dark current.²⁴ One of the problems encountered when using polyimide for encapsulation is its poor gap filling characteristics, due to insufficient wetting, high viscosity, and high extent of shrinking during curing.⁴ Some improvement in its gap-filling properties can be obtained by vacuum drying,²⁵ nevertheless there is still a need for a proper method that will provide both surface passivation and high quality encapsulation.

In this article a new approach for obtaining both surface passivation and high quality encapsulation is proposed. This approach is based upon surface passivation of InP-based microelectronic devices by tailored thiolated SAMs, which not only form chemical bonds with the semiconductor, but also serve as adhesion promoters for a polyimide encapsulator.²⁶

II. EXPERIMENT

Three types of samples were used, all of which were coated with thiolated self-assembled monolayers (SAMs): InP wafers, metal–semiconductor–metal (MSM) photodiodes, and *p-i-n* photodiodes. In order to examine compatibility with existing encapsulating processes, part of the samples were coated with polyimide layers (0.5–0.7 μm thick) by spin-on coating (5000 rpm, 1 min) using a 1:1 (v/v) solution of Pyralin™ 2555 (DuPont) and a commercial thinner.

(a) InP wafers. S-doped, *n*-type InP (100) wafers were used to characterize the quality of the SAMs used in this work and for photoluminescence experiments. The wafers were coated with various thiolated SAMs by a method similar to that of Gu and Waldeck.²⁷ Four types of SAMs were studied: octadecyl mercaptan [ODT, $\text{CH}_3(\text{CH}_2)_{17}\text{SH}$], mercapto-hexadecanoic acid [MHDA, $\text{HS}(\text{CH}_2)_{15}\text{COOH}$], mercapto-undecanoic acid [MUDA, $\text{HOOC}(\text{CH}_2)_{10}\text{SH}$], and mercapto-undecanol [MUD, $\text{HO}(\text{CH}_2)_{10}\text{SH}$]. The coating procedure consisted of ultrasonic cleaning with organic solvents (acetone, methanol, and isopropanol consecutively), immersion in a concentrated HF solution (49%, 5 min.), and rinsing with water and isopropanol. Subsequently, the samples were immersed in the alkanethiol-containing solution (0.1 M in very large scale integrated grade isopropanol, 65 °C) for 12–30 h in nitrogen ambient, and then rinsed several times with hot isopropanol.

(b) Metal–semiconductor–metal (MSM) diodes. The MSM diodes used for this work were shaped as interdigitated electrodes [Fig. 1(A)]. The preparation scheme consisted of etching Fe-doped InP by concentrated hydrofluoric acid (49%, 1 min ambient temperature) to remove the native oxide, followed by a standard “lift-off” process, which ended with two finger-like Ti/Au electrodes. The metal “fingers”

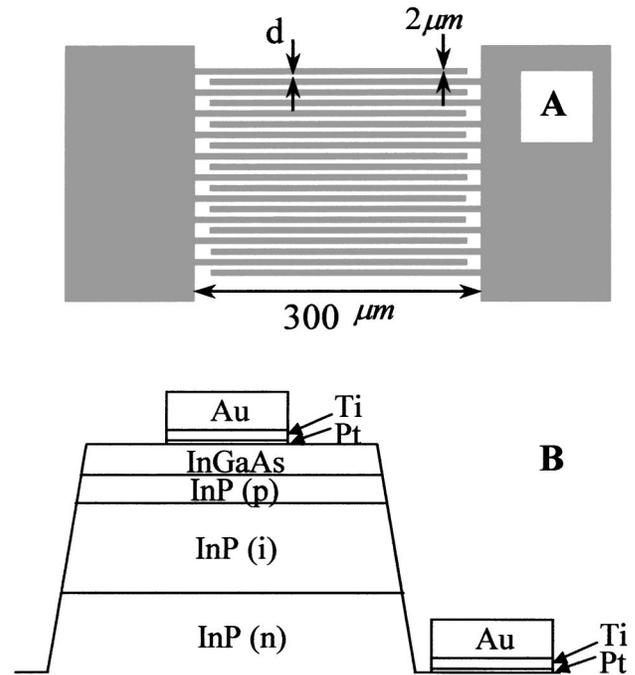


Fig. 1. (A) Schematic top view of the MSM diode structure. (B) Schematic side view of the *p-i-n* photodiode structure.

were 2 μm wide and 300 μm long. Four types of diodes having different interelectrode spacings (d) were used: 2, 4, 6, and 8 μm . The passivation of the MSM diodes with monolayers of ODT and MHDA was performed in the same manner described for the InP wafers, except for an additional oxygen plasma-ashing step, immediately after the “lift-off” process, in order to remove adsorbed organics. In addition, the HF treatment, previously used for plain wafers to remove the native oxide, was replaced with short etching by an aqueous solution of 37% HCl and 86% H_3PO_4 (3:1 v/v, 5 °C, 3 s), to avoid titanium layer etching.

(c) *p-i-n* photodiodes. The layers were grown by a compact metalorganic molecular beam epitaxy system similar to a system described before.²⁸ Trimethylindium, triethylgallium, arsine, and phosphine served as group III and V sources. Solid tin and beryllium served as *n*-type and *p*-type dopant sources. Carbon tetra-bromide served as an additional *p*-type carbon dopant source. The layers structure, shown in Fig. 1(B), consisted of an *n*-type S-doped InP substrate, a 300 nm thick Sn-doped InP layer, a 100 nm thick *p*-type Be-doped InP layer, and a 100 nm thick heavily doped *p*-type InGaAs contact layer. Patterning included InGaAs etching in $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:8:100 v/v/v) solution, and InP etching in $\text{HCl}:\text{H}_3\text{PO}_4$ (1:3 v/v). Three-layered ohmic contacts (10 nm Pt, 40 nm Ti, 200 nm Au) were evaporated and patterned by a conventional lift-off technique.

Steady state photoluminescence of coated and noncoated wafers was measured by exciting the surfaces with a He–Ne laser light, and directing the luminescence signals through a Digikrom 240 monochromator to a Ge-detector (EO-817L, N.C. Scientific Corp.). The current–voltage characteristics of both passivated and nonpassivated diodes were measured by

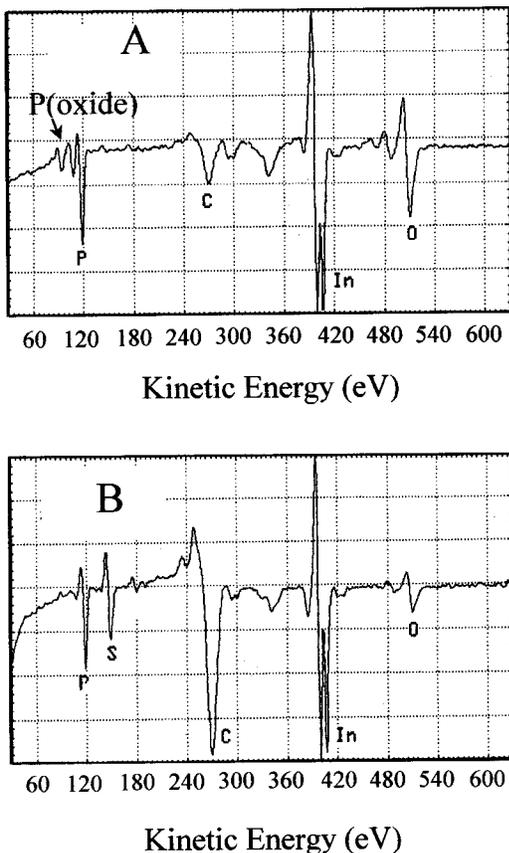


FIG. 2. Auger spectra of untreated InP (A) and InP coated with ODT (B).

a HP-4145B SPA. Due to the well-known tendency of gold to chemisorb thiolated molecules, care was taken to clean the contacts prior to measurements. This was done by oxygen plasma ashing while protecting the rest of the sample by patterned photoresist, later to be removed.

To minimize the effect of wafer-to-wafer inhomogeneity on the experimental results, care was taken to perform comparative photoluminescence measurements only with samples taken from the same wafer.

III. RESULTS AND DISCUSSION

A. Characterization

Figure 2 presents Auger spectroscopy results of a bare InP wafer (A) and of an ODT-coated InP wafer (B). Both wafers were HF treated together right before coating, which took place three days prior to the Auger measurements. The carbon and sulfur signals are evident in the ODT-coated wafer. The amount of oxygen in the coated wafer is clearly less than in the bare wafer, and no indication for oxidized phosphorous can be found. This is not the situation in the bare InP, where oxidized phosphorous peaks can be observed at lower kinetic energies relative to bulk phosphorous. Hence it can be concluded that coating InP with thiolated self-assembled monolayers prevents oxygen penetration into the semiconductor, at least for a few days. Characterization of ODT monolayers on InP wafers by angle resolved XPS gave re-

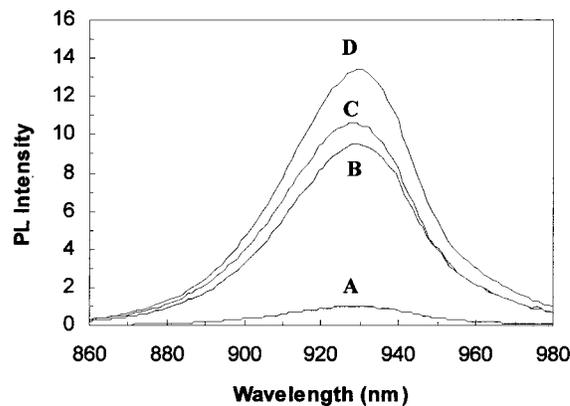


FIG. 3. Photoluminescence spectra of indium phosphide wafers: (A) untreated wafer, (B) coated with ODT, immersion time: 17 h, (C) coated with ODT, immersion time: 24 h, and (D) coated with ODT, immersion time: 30 h.

sults similar to those published by Gu *et al.*,²⁷ i.e., demonstrated the existence of an organic layer with a thickness of 17 ± 2 Å and suggested a chemical bonding between the sulfur of the ODT and the indium atoms of the semiconductor.

InP wafers coated with SAMs were characterized by Fourier-transform infrared (FTIR) spectroscopy in the transmission mode, using a Bruker IFS55 machine. The $\text{CH}_2(\text{a})$, $\text{CH}_2(\text{s})$, and $\text{CH}_3(\text{a})$ peaks were identified at 2920, 2850, and 2960 cm^{-1} , respectively. These values, as well as the intensity of the peaks, are in line with those obtained for the same monolayers on Au (Ref. 29) and GaAs.¹³ The modified surfaces were characterized also by wettability measurements with water. Here, the advancing contact angle on an untreated InP surface, InP coated with ODT, and InP coated with MHDA were 55°, 105°, and 17°, respectively. These values demonstrate the effect of the outer functional group of the monolayer, as expected for densely packed structures.

B. Steady state photoluminescence of InP wafers

Figure 3 presents the photoluminescence spectrum of an

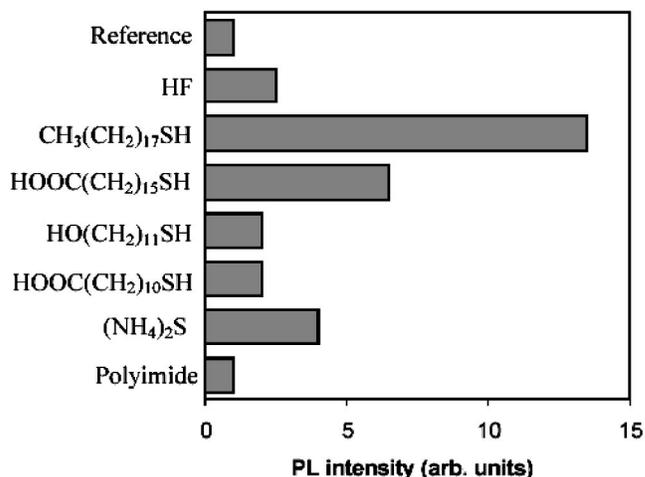


FIG. 4. Photoluminescence intensity at 928 nm of indium phosphide wafers following various treatments.

untreated n-type wafer of indium phosphide (A), and of three other wafers that were coated with an ODT monolayer at different immersion times (17, 24, and 30 h). A clear enhancement of the photoluminescence (PL) intensity of the treated samples is observed. The larger the immersion time was, the higher the PL intensity was. For an immersion time of 30 h an increase by a factor of 14 was obtained.

In Fig. 4 the PL intensity measured at 928 nm for InP wafers coated with various SAMs is presented. For clarity, results are given relatively to the PL of an untreated wafer. As presented in the figure, etching the InP by HF, a process that strips the wafer from its oxide, increased the PL signal by a factor of 3. Nevertheless, this enhancement in the signal disappeared after a short time, probably due to reoxidation by ambient air. Similarly, coating etched wafers with thin (500 nm) layers of polyimide, a traditional material for encapsulation of InP-based devices, did not yield any improvement in the PL signal relative to bare wafers.

The effect of coating with SAMs on the PL intensity was found to depend mainly on the length of the alkyl chain. The longer the chain was, the higher the PL intensity was. SAMs having alkyl chains made of 10 or 11 methylene groups yielded very small improvement in the PL intensity, whereas ODT, with its 17 methylene groups, increased the PL signal by a factor of 14. For comparison, HF-etched InP wafers that were immersed in 20% $(\text{NH}_4)_2\text{S}$ solution for 24 h, and measured within 30 min yielded an increase in their PL signal by no more than a factor of 3 to 4. The difference in the PL intensity between wafers coated with short chain SAMs and wafers coated with long chain SAMs can be explained not only on the basis of the increased thickness of the protective layer but also on the improved packing of long chained monolayers due to a larger number of interchain van der Waals interactions. It is of interest that the photoluminescence intensity of ODT-coated InP wafers, measured several days after preparation, was three times higher than that of InP wafers that were HF treated just before measuring. This suggests that the increase in the PL signal following coating was mainly due to surface passivation and not due to the limitation on the mass transfer of oxygen from the air to the semiconductor.

The coating of the InP surfaces by close-packed organic monolayers attached covalently to the surface reduces the number of dangling orbitals and at the same time creates a physical barrier for the penetration of oxygenating species, as can be inferred from the Auger spectroscopy results. The fact that the photoluminescence of freshly etched InP wafers was enhanced by no more than 200% upon HF treatment, while coating with a monolayer of ODT yielded an enhancement of 1300% in the PL signal, suggests that the main factor in the photoluminescence experiments is not the prevention of oxidation but rather the decrease in the number of dangling bonds. Within this context, it is noteworthy to mention that etched wafers coated with a layer of a commercial polyimide encapsulator, that prevents penetration of oxygen but does not form chemical bonds with the surface, hardly increased the photoluminescence signal. It is important to

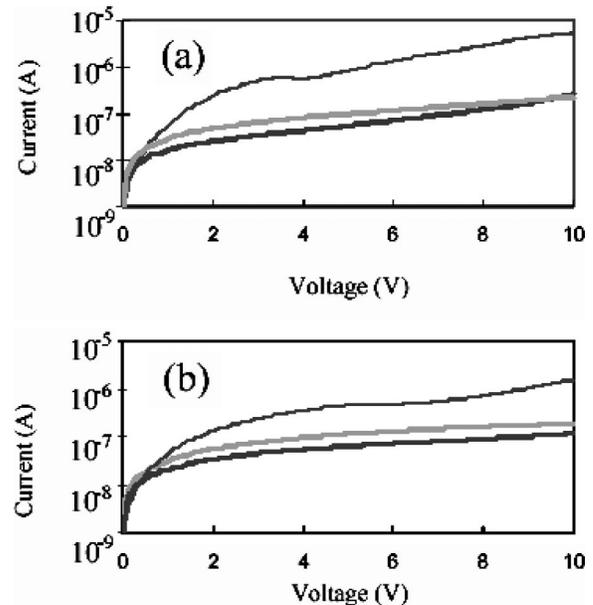


FIG. 5. Dark current of MSM diodes with different interelectrode spaces d : (a) $d = 2 \mu\text{m}$ and (b) $d = 4 \mu\text{m}$. The thin black lines represent untreated diodes, bolded gray lines represent diodes passivated by MHDA, and black bold lines represent diodes that were passivated by ODT.

clarify that increased photoluminescence, as a method for characterizing passivation, depends heavily on the thickness of the semiconductor layer. Since radiative recombination is mostly a bulk phenomenon, the thinner the semiconductor is, the more pronounced the effect of the depletion layer near the surface is, hence it is expected to have a larger difference in the PL intensity of a passivated semiconductor in comparison with a nonpassivated one. For example, passivation of GaAs wafers 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,³⁰ while the same passivator increased the PL intensity of a $1 \mu\text{m}$ GaAs epilayer by a factor of 270.¹⁵ Hence, the 14 times increase in the PL intensity of InP wafers due to their coating with the ODT monolayer clearly represents a significant passivation effect.

C. Dark current measurements of InP MSM diodes

Figure 5 presents the dark current measurements of InP MSM diodes, passivated by ODT and MHDA monolayers. For comparison, the dark-current characteristics of the same type of diodes, but without any coating, is also given. It is clearly observed from the I - V plots that covering the surface of these diodes by thiolated SAMs reduces by more than an order of magnitude their dark currents. This effect is slightly more pronounced in diodes having an interelectrode spacing of $2 \mu\text{m}$ [Fig. 5(a)] than in diodes having an interelectrode spacing of $4 \mu\text{m}$ [Fig. 5(b)] or larger.

The decrease in the leakage current of the MSM diodes following their coating by thiolated SAMs is obviously the result of passivation of their surface, since, in general, there is a well-known connection between the presence of surface states and injection of charge carriers.³¹ This conclusion is

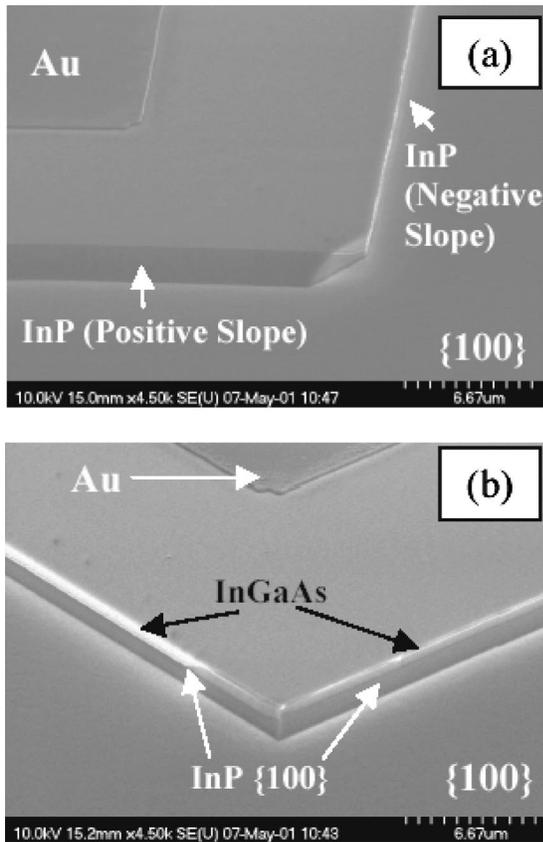


FIG. 6. SEM images of the *p-i-n* photodiodes: (a) “parallel” orientation and (b) “diagonal” orientation.

supported by the observation that polyimide coating, which prevents oxidation but does not form chemical bonds with the surface, did not reduce leakage. Comparing our results to those obtained by other methods is difficult because of the different electrode geometries used in previous publications. However, the leakage current per unit length of the electrodes at a given electric field provides a normalized basis for comparison. When such a comparison is made, one finds that passivation by this method is comparable to passivation by an ammonium polysulfide treatment,³² and is superior to passivation by SiO_2 .³¹ As presented in Fig. 5, MSM diodes covered with ODT were more effective than diodes covered with MHDA. This result, which was found also in other sets of MSM diodes, is consistent with the photoluminescence measurements described before, and explained by the better compactness and order of the longer chain monolayer, in line with observations of organo-thiolated monolayers on gold.³³

D. Passivation of *p-i-n* photodiodes

In microelectronic devices produced by a nonplanar technology, the active surfaces that may require passivation are often the mesas’ sidewalls, whose orientation may vary according to the geometry of the mesa.²² *p-i-n* avalanche photodiodes and the collector in a heterojunction bipolar transis-

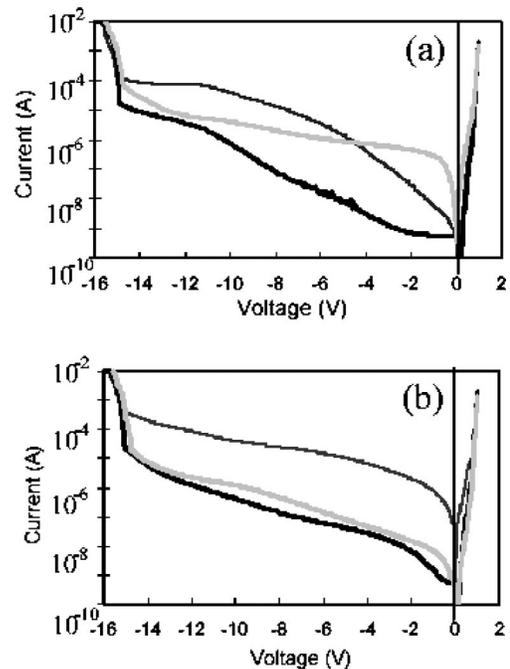


FIG. 7. Dark current measured for *p-i-n* photodiodes under reverse bias: (a) “parallel” orientation and (b) “diagonal” orientation. The thin black lines represent untreated diodes, bolded gray lines represent diodes passivated by polyimide, and black bold lines represent diodes that were passivated by ODT.

tor are examples of such devices, where the surface that requires passivation is the outer area of the intrinsic layer on the walls of the mesa.

The passivation of *p-i-n* avalanche photodiodes (APDs) by thiolated SAMs was studied in two types of identical rectangular photodiodes ($180 \times 270 \mu\text{m}^2$), which differed only by their direction relative to the wafer flat: one was parallel to the flat, while the other (termed hereby as “diagonal”) was directed 45° relative to the flat. SEM images of these devices (Fig. 6) revealed a distinct difference between the two orientations. In the parallel-type devices the couple of sidewalls which were parallel to the flat (indexed as $\langle 1, -1, 0 \rangle$) had positive slopes, indexed as $\{111\}$, while the walls perpendicular to the flat had negative slopes, of higher indices. In contrast, the sidewalls in diagonal-type devices were found to be perpendicular to the (001) plane of the wafer, hence belonging to the $\{100\}$ family of planes.

The effect of passivation with ODT monolayers was studied by measuring $I-V$ curves in the dark under reverse bias. Typical results for the two types of orientations are given in Fig. 7. For comparison, the $I-V$ curves in nonpassivated devices and in devices coated by a layer of polyimide are presented as well.

A distinct difference between the $I-V$ curves of the two types of “naked” diodes is clearly observed. Evidently, the dark current of the “parallel” APD is lower than the dark current of the “diagonal” APD. This difference, which is more pronounced under low bias, can be explained by the difference in the sidewalls planes of the two configurations that gives rise to a different number of surface dangling

bonds, hence to a variation in the electrical resistivity of the surface. This issue, which can be relevant to many types of microelectronic devices that are produced by nonplanar technology, is somehow overlooked and definitely deserves an in-depth study. Coating with a layer of polyimide seems to decrease the parasitic current to some extent, especially in devices directed 45° relative to the $\langle 1, -1, 0 \rangle$ direction of the wafer's flat. Here, the difference between the two orientations can be explained by the negative slopes of two of the sidewalls in the parallel configuration, which may cause the formation of air pockets during coating. As presented in Fig. 7, a decrease in the reverse bias current by up to two orders of magnitude was obtained upon coating with the thiolated monolayers. Similar to the previous examples, this reduction in leakage can be attributed to a decrease in the number of the dangling orbitals due to the chemical interaction between the passivant and the semiconductor, which affects the number of mid-band-gap surface states. A difference was observed between the two configurations, where the parallel configuration yielded lower dark currents. This suggests, but does not prove, not only that the negative slopes in the parallel configuration do not prevent wetting by the isopropanolic coating solution, but also that alkylthiolated monolayers on non- $\{100\}$ planes are more compact than monolayers on $\{100\}$ planes. Such a difference is expected if one takes into consideration that the sulfur tends to be bonded to two vicinal indium atoms,⁸ and that the distance between adjacent indium atoms depends on the crystalline plane. A detailed work on the effect of InP crystalline planes on the properties of organothiolated monolayers is underway.

E. Compatibility with polyimide encapsulation

As mentioned above, good adherence between the polyimide encapsulator and the surface of the microelectronic device is essential, otherwise deterioration in the electronic performance might occur due to penetration of oxygen or humidity. The problem of coating is aggravated in undercuts and in negative slopes sidewalls, where gas microbubbles may form due to the lack of sufficient wetting of the device by the encapsulator. The previous sections demonstrated that organothiolated monolayers can serve to passivate the surface of InP. Nevertheless, these layers are too thin to provide adequate protection against humidity and oxygen, unless they are covered with a compatible encapsulating layer. Such a compatibility between thiolated SAMs and polyimide is discussed hereby.

Table I presents the advancing contact angles of Pyra-

TABLE I. Advancing contact angles on ODT-coated InP and on MHDA-coated InP of a commercial polyimide solution (pyralinTM), its thinner, and a pyralinTM-thinner (1:1 v/v) solution often used for planarization.

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

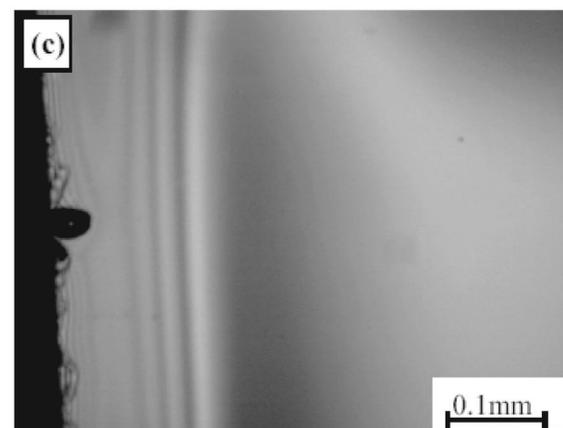
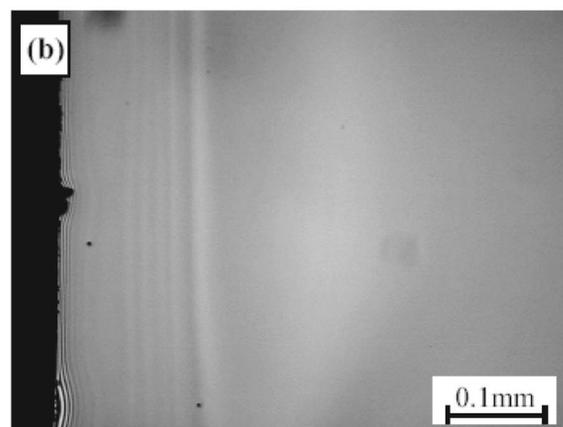
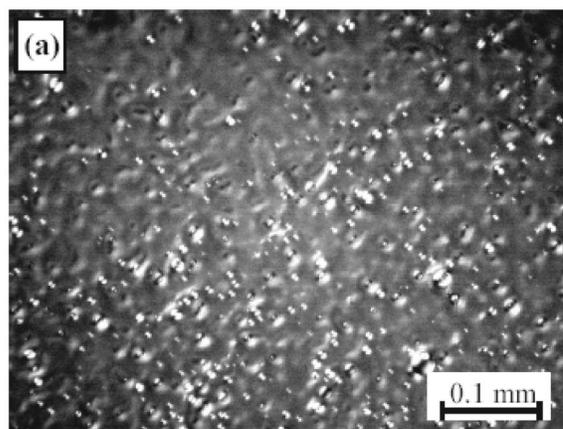


FIG. 8. Optical microscopy images of a spin-coated layer of a commercial polyimide encapsulator (pyralinTM) on: (a) ODT-coated InP wafer, (b) MHDA-coated InP wafer, and (c) MHDA coated InP wafer, following the curing of the encapsulator.

linTM, a commercial polyimide encapsulator for III–V devices, without and with 1:1 (v/v) thinning by a commercial thinner, as measured on bare InP surfaces, and on InP surfaces that were modified by monolayers of ODT and MHDA. The effect of surface treatment on the extent by which the surface is wet is clearly demonstrated. Coating with ODS, a monolayer consisting of molecules having nonpolar outer groups, yields an advancing contact angle of 55° with PyralinTM, 20° higher than the contact angle on bare InP, while coating with MHDA, a COOH-terminated chain, yields a

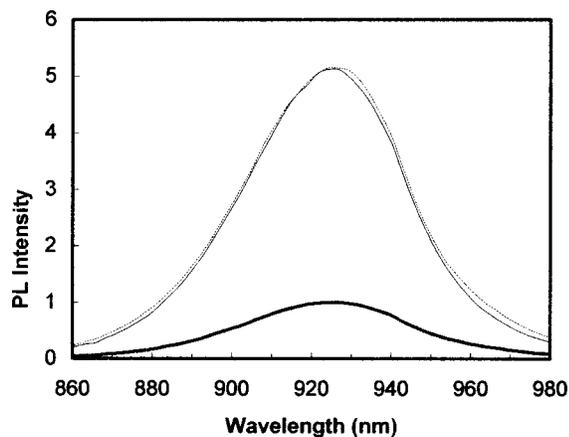


FIG. 9. PL spectrum of bare InP wafer, (thick line), MHDA-coated InP wafer (dashed line), and MHDA-coated InP wafer, having a cured polyimide overcoating (thin line).

significant reduction in the contact angle. This reduction can be attributed to the formation of hydrogen bonds between the carboxylic acid at the outer part of the monolayer and C=O groups in polyimide. Figure 8 presents optical microscope imaging of polyimide on ODT-coated (a) and on MHDA-coated (b) InP wafers. As shown, polyimide on an ODT-coated wafer forms an inhomogeneous coating, made of separate islands due to dewetting between the hydrophilic polymer and the hydrophobic outer group of the ODT. In contrast, polyimide on an MHDA-coated InP wafer forms a smooth, evenly spread, homogeneous layer. It is well known that uncovered, air-exposed thiolated SAMs on gold show significant lateral mobility already at 100 °C can be totally removed, leaving behind an uncovered gold surface at a temperature of 130 °C.³⁴ Since present encapsulating technology utilizes polyimides that require a curing temperature as high as 200 °C, the question of compatibility between passivation by thiolated SAMs and the existing encapsulation process is not trivial. Indeed, when the temperature of ODT-coated InP was raised to 200 °C and was kept at that temperature in air for no more than 10 min, a significant decrease in the contact angle of water, from 105° to 60°, and a disappearance of the FTIR signal of the monolayer were observed. In contrast, high temperature (250 °C, 2 h) curing of polyimide spread on MHDA did not affect the quality of the polyimide layer, as is evidently shown in Fig. 8(c). To reassure that the improved electrical properties obtained by coating with SAMs are not damaged by the high temperature curing of the encapsulator, the photoluminescence of InP passivated by MHDA and overcoated by Pyralin™, prior to and after curing, was measured (Fig. 9). Results are compared also with the photoluminescence of an untreated wafer. Evidently, the enhanced PL intensity upon the passivation by the MHDA was not damaged at all following curing, and was approximately five times higher than in the untreated wafer. The stabilization of the monolayer at elevated temperatures by the polyimide can be explained by the monolayer's restriction of movement due to the overcoating. Another mechanism may be related to the quality of the encapsulator as a barrier for oxygen diffusion,

since thermal deterioration of organothiolated SAMs is known to be connected with oxidation of the thiolate species.³⁴

IV. CONCLUSIONS

The effect of modifying the surface of InP devices by thiolated self-assembled monolayers on their optoelectronic properties was demonstrated by three examples: photoluminescence of InP wafers, dark current under negative bias in interdigitated metal–semiconductor–metal diodes, and reverse bias current in *p-i-n* diodes. Evidently, the thiolated SAMs reduce significantly (in certain cases by up to two orders of magnitude) the rate of nonradiative recombination at the surface. This is done by removing natural oxide and the prevention of reoxidation, as well as by reducing the number of dangling orbitals and, as a consequence, also the number of surface states.

The extent by which the thiolated SAMs affect the optoelectronic properties depends not only on the type of the electronic devices and their dimensions, but mainly on the quality of the monolayer. Accordingly, shorter-chain molecules, as well as molecules with an outer groups that are bulkier than the alkyl backbone, had an inferior passivation effect in comparison with longer-chained molecules having a methyl outer group.

Layered *p-i-n* diodes, where the dark current flows through the sidewalls of the mesas, reveal another, frequently overlooked, factor. The fact that the crystalline planes of the sidewalls depend on the orientation of the device relative to the $\langle 1, -1, 0 \rangle$ direction of the wafer's flat affects surface non-radiative recombination through the exposure of surfaces that are structurally and electronically different, as well as through the formation of negative slopes. The former is closely related to passivation, while the latter is related mainly to encapsulation, in particular to encapsulation by viscous polymers. More work on this topic is underway.

The main benefit of coating InP-based electronic devices with thiolated SAMs is the potential of using these passivants together with standard encapsulators such as polyimides. The possibility of using monolayers having outer groups that are compatible with polyimides and the fact that the high temperature curing of the polymers does not damage the SAMs underlayer provides a good basis to propose that such an attitude is feasible. That way, it is hoped to provide high quality passivation and encapsulation, even when the electronic devices contain sidewalls having negative slopes or undercut cavities.

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