



## Surface localization of the photochemical vapor deposition of SiO2 on InP at low pressure and room temperature

F. Houzay, J. M. Moison, and C. A. Sébenne

Citation: Applied Physics Letters **58**, 1071 (1991); doi: 10.1063/1.104374 View online: http://dx.doi.org/10.1063/1.104374 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/58/10?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in Lowtemperature metalorganic chemical vapor deposition of InP on Si(001) Appl. Phys. Lett. **58**, 284 (1991); 10.1063/1.104662

A combination of rapid thermal processing and photochemical deposition for the growth of SiO2 suitable for InP device applications J. Appl. Phys. **68**, 5636 (1990); 10.1063/1.346976

Effect of substrate temperature on the properties of SiO2/InP structure prepared by photochemical vapor deposition J. Appl. Phys. **67**, 3350 (1990); 10.1063/1.345372

Heteroepitaxial growth of InP directly on Si by low pressure metalorganic chemical vapor deposition Appl. Phys. Lett. **50**, 1725 (1987); 10.1063/1.97728

Growth of ultrapure and Sidoped InP by low pressure metalorganic chemical vapor deposition Appl. Phys. Lett. **46**, 476 (1985); 10.1063/1.95562



## Surface localization of the photochemical vapor deposition of SiO<sub>2</sub> on InP at low pressure and room temperature

F. Houzay and J. M. Moison

Laboratoire de Bagneux,<sup>a)</sup> Centre National d'Etudes des Télécommunications, France Télécom, 196 Avenue Henri Ravera, F-92220 Bagneux, France

C. A. Sébenne

Laboratoire de Physique des Solides, Université Pierre et Marie Curie, 4 Place Jussieu, F-75005 Paris, France

(Received 24 July 1990; accepted for publication 7 December 1990)

The first stages of the chemical vapor deposition of  $SiO_2$  on chemically polished InP substrates, promoted by UV illumination at room temperature and low ( $\approx 0.01$  Torr) precursor pressure, have been studied in an ultrahigh vacuum environment. Chemical species deposited are found to be quite similar to those deposited by the thermally promoted process. Both Si and O atom depositions need UV illumination. The reaction rates observed in separate or mixed gas exposures indicate that surface-located mechanisms play a major part in the buildup of the SiO<sub>2</sub>/InP interface at low precursor pressure, thus opening perspectives for localized insulator growth under the UV beam.

Deposition of dielectrics on III-V semiconductors for the fabrication of devices is mainly achieved by chemical vapor deposition (CVD). In order to decrease growth temperatures which may damage the substrates, cold CVD techniques, promoted by plasma or ultraviolet illumination (UVCVD) have been devised.<sup>1</sup> CVD from the lowpressure precursor gas combination  $(SiH_4 + O_2)$  assisted by the 185 nm radiation of a Hg lamp is one such technique.<sup>2</sup> It has the further potential interest of allowing localized deposition, or direct writing of insulator patterns. The resolution of this patterning is linked to the growth mechanism: in gas-phase reactions, the diffusion of the products can blur the pattern, while for surface-located reactions the growth pattern reproduces the UV illumination pattern. In spite of the importance of the issue, only tentative discussions have been disclosed.<sup>3</sup> We present here evidence obtained from in situ studies of the occurrence of surface-located reactions during the first stages of the UVCVD growth of SiO<sub>2</sub> on InP at room temperature and low precursor pressure (0.01 Torr). The influence of the pressure on the location of the reactions is discussed.

Experiments were carried out in an ultrahigh vacuum chamber equipped with Auger electron spectroscopy (AES) and x-ray photoemission spectroscopy (XPS).<sup>4,5</sup> (100)InP wafers with a low *n*-type bulk doping ( $\approx 10^{16}$ cm<sup>-3</sup>) were slightly chemomechanically polished and rapidly introduced via load lock in the reaction chamber. SiH<sub>4</sub> and/or  $O_2$  gas pressures laid in the  $10^{-2}$  Torr range, and exposure times in the 1000 s range, thus giving exposures in the  $10^7$  Langmuir range 1 L =  $10^{-6}$  Torr s). During exposures, all filaments and voltages inside the chamber were turned off. The UV illumination was provided by a Hg lamp (185 and 254 nm) which illuminated homogeneously the sample surface. The fluence was estimated at 0.05 mW/cm<sup>2</sup> at 185 nm from the measurement of the  $\approx 1$  $\mu$ A/cm<sup>2</sup> current photoemitted by the sample,<sup>6</sup> i.e., a quite small value.

After each exposure, XPS (see Fig. 1) and AES spectra were taken. Complete sets of spectra will be reported elsewhere.<sup>6</sup> The deduction of Fermi level shifts from those of the substrate core levels In 4d and P  $2p^{4,5}$  allowed us to zero the energy scale for deposit Si and O peaks at the valence-band maximum, thus keeping only chemical shifts. The area of these peaks referred to the one of In 4d was taken as a measurement of the silicon and oxygen coverage  $(\theta_{Si}, \theta_{O})$ .<sup>4,5</sup> From the analysis of standards, and values of escape depths,<sup>7</sup> and photoionization cross sections,<sup>8</sup> we estimated Si  $2p/\text{In } 4d = 0.048 \pm 0.010$ and O 1s/ In  $4d = 0.18 \pm 0.04$  for the monolayer coverage (1 ML) defined as the atom density  $(N_s = 5.844 \times 10^{14} \text{ cm}^{-2})$  in the (100) plane of InP. Finally, the deposition efficiency, defined as the ratio of adsorbed coverage (ML) to exposure (L), was deduced.

The starting surface reproducibly contains about 2.5 ML of oxygen;<sup>5</sup> its carbon contamination is stable throughout further treatments and will not be discussed here. Without UV illumination, no appreciable change—in particular, no Si or O uptake—is observed following exposures at room temperature to either gas or mixture up to  $10^9$  L. On the opposite, with UV illumination, we do observe Si and O uptakes following alternate exposures to SiH<sub>4</sub> and O<sub>2</sub> from about  $10^7$  L.

Low SiH<sub>4</sub> exposures build up a submonolayer Si coverage, as seen by XPS and AES.<sup>6</sup> According to literature data<sup>9</sup> and our standards, XPS indicates a SiO<sub>2</sub>-like bonding, seen on both Si 2p and O 1s peaks. In parallel, the native oxygen—InP bonds are nearly completely reduced, as seen from the disappearance of the In-O-P XPS peak<sup>10</sup>, of the AES peak associated with P—O bonds, and of the In-O components of the In *KLL* AES peak.<sup>6</sup> The reduction of the native oxide to form the first SiO<sub>2</sub> clusters is similar to the one observed during the hot CVD process:<sup>4</sup> Si atoms insert between InP and oxygen atoms, thus turning the interface bonding to the "covalent-like" InP-Si-Oconfiguration. Further SiH<sub>4</sub> exposures increase the Si coverage, but its bonding clearly changes, with the appearance of less oxidized forms, perhaps down to the Si—Si covalent

<sup>&</sup>lt;sup>a)</sup>Laboratoire de Bagneux is Unité Associée au C.N.R.S. UA250.



FIG. 1. Evolution upon successive gas exposures under UV illumination of Si 2p and O 1s XPS peaks referred to the valence-band edge. Energies corresponding to the Si oxidation states are derived from Ref. 9. Peaks are roughly decomposed into Gaussian components with full width at half maximum 2.3 eV for O 1s and 2.4 eV for Si 2p.

bonding. The silicon deposited first takes up the oxygen of the native oxide to form near-SiO<sub>2</sub> groups; when those bonds are exhausted, it tends to adsorb as covalent Si. In parallel, the deposition efficiency decreases from  $3 \times 10^{-8}$ at zero Si coverage down to  $5 \times 10^{-9}$  at 1.5 ML. Figure 2 shows this evolution as a function of surface stoichiometry, averaged by  $\theta_{Si}$ - $\theta_{O}$ .

Following  $O_2$  exposures again oxidize the Si atoms present at the surface nearly to the SiO<sub>2</sub>-like state, as seen from the disappearance of the low-energy components to the XPS peak and of the  $\approx$ Si AES peak.<sup>6</sup> The substrate is slightly oxidized again, as seen from the reappearance of the In-O-P XPS peak and confirmed by the one of the P-O AES peak, and of the In-O components of the In *KLL* AES peak.<sup>6</sup> A new bonding state of oxygen intermediate between P—O—In and O—Si appears, which can be attributed to O bonding to both InP and Si following the reoxidization of the InP substrate. This shows that the



FIG. 2. Deposition efficiency vs average surface stoichiometry  $\theta_{Si}$ - $\theta_{O}$ .

SiO<sub>2</sub>-like layer formed is not uniform. The deposition rate of oxygen is found to be similar to the one of silicon,  $\approx 3 \times 10^{-8}$  for a Si-rich surface; for O-rich surfaces, this coefficient vanishes (Fig. 2).

Combined exposures to 1:1 mixtures of the two gases lead to a simultaneous O and Si uptakes. Adsorbed species are the same as the ones observed for alternate exposures. The Si deposition rate referred to the partial pressure of SiH<sub>4</sub> is found to be  $\approx 1 \times 10^{-7}$ , i.e., about three times the one observed after exposures to SiH<sub>4</sub> alone. This corresponds to a growth rate of  $\approx 10$  Å/h at 0.01 Torr and 0.05 mW/cm<sup>2</sup> UV fluence. We tested for the existence of charged photofragments in the gas phase during mixed exposures by studying the *I-V* curve of the sample/ground diode. This curve does not depend on the gas pressure and reveals only the photoemission current, from which we deduce the photon flux as mentioned earlier. No significant variation of the reaction efficiency with the sample bias is observed either.

For the mixed exposures which are the rule in UVCVD, many reaction paths must be considered. For medium-pressure CVD (>10 Torr), a purely gas-phase scheme has been devised on the basis of gas-phase adsorption data:<sup>12</sup> O<sub>2</sub> only is photodissociated to O or O<sub>3</sub> radicals which then react with  $SiH_4$  to give  $SiO_xH_\nu$  radicals which aggregate and/or stick to the substrate. At lower pressures, partly or totally surface-located schemes have been suggested to become dominant.<sup>3</sup> Examples of such schemes are: (i) photogeneration of  $SiH_n$  and/or O/O<sub>3</sub> radicals in the gas phase followed by reaction at the surface with either the other radical or with the other species already present, and (ii) adsorption of both molecular species at the surface and reaction with other radicals or species already present promoted in situ by UV light. This last scheme is coherent with our experimental observations as follows:

(i) the comparatively small difference between deposition efficiencies for separate or mixed exposures, which may be attributed to the constant arrival at the surface of the other species during mixed exposures, and which indicates that mechanisms are the same in both cases;

(ii) the similar deposition efficiencies of photopromoted UV deposition of Si under SiH<sub>4</sub> exposure and O under O<sub>2</sub> exposure compared to the very different gasphase cross sections,<sup>12</sup>

(iii) the strong dependence of these efficiencies on the surface composition;

(iv) the similarity of species deposited by UVpromoted and hot thermally promoted processes.<sup>4</sup>

The nonobservation of charged photofragments in the gas phase, which should go with the creation of radicals, also confirms the surface localization of the process. These observations, together with the very strong dependence on substrate temperature of the growth rate in UVCVD,<sup>2</sup> also point to a photoexcitation mechanism different from a simple excitation of adsorbed molecules and mediated by the substrate as in the hot process.

This conclusion may be confirmed by an estimation of deposition efficiencies in various schemes. Whatever the

supplique a de malectera en la construction de la c



FIG. 3. Evolution with precursor pressure of the deposition rate for various reaction paths (GG,GS,SS); experimental values for separate (resp. mixed) exposures are represented as open (resp. full) squares.

actual reaction path, it involves a photodissociation step, which breaks molecules into radicals, and a reaction step which groups radicals and/or molecules to form  $SiO_x$  clusters. We consider three schemes with various locations for these steps: (i) photodissociation and reaction in the gas phase (GG), (ii) photodissociation in the gas phase and reaction at the surface (GS), and (iii) both steps at the surface (SS). We evaluate the deposition efficiency upon mixed exposures with the following assumptions. For the GG path, a radical created by UV photodissociation with a cross section  $\sigma_d$  can react along its path L-smallest between mean free path and lamp-sample distance ( $\approx 1$  cm in our case)-reacts with the other molecule with a cross section  $\sigma_r$  and adsorbs on the surface with a unity probability.<sup>12</sup> For the GS path, the dissociation step is similar, but the radical sticks to the surface with a unity probability and reacts here with already present species. For the SS path, molecules adsorb with a stationary coverage  $\theta$  described by a Langmuir adsorption isotherm<sup>13</sup> with energy E. For a homogeneous photon flux  $J_{ph}$ , we end up with the following efficiencies:

 $(GG)J_{ph}\sigma_d nL\sigma_r nL/(10^6 PN_s),$   $(GS)J_{ph}\sigma_d nL(1-\sigma_r nL)/(10^6 PN_s)$  $(SS)J_{ph}\sigma_d \theta/10^6 P,$ 

where P is the pressure in Torr and n the molecular density in the gas. The evolution of those efficiencies with pressure at our photon flux  $J_{ph} = 5 \times 10^{13}$  cm<sup>-2</sup> s<sup>-1</sup> is shown in Fig. 3 for  $\sigma_r = 10^{-15}$  cm<sup>2</sup>,  $\sigma_d = 1 \times 10^{-17}$  cm<sup>2</sup>, and E = 0.6 eV.<sup>12</sup> With these values, the model predicts low pressure efficiencies in the dominant SS regime in fair agreement with experimental values, and also a switch to the GG regime above 10 Torr. The comparison between GG and the other schemes depends mainly on  $\sigma_r$ , for which we took a maximal value, thus favoring GG which nevertheless remains much less efficient than GS or SS at low pressure. The comparison between GS and SS depends mainly on E, which is not accurately known; considering the experimental indications, the value  $\ge 0.6$  eV is reasonable, thus predicting the surface photodissociation to be always faster than the gas-phase one.

In conclusion, we have studied the first stages of the deposition of SiO<sub>2</sub> on InP by UV-promoted CVD at room temperature and low precursor pressure ( $\approx 0.01$  Torr). The chemical products and the steps of the reaction path are very similar to those obtained in the hot CVD process. Both the deposition of Si from  $SiH_4$  and of O from O<sub>2</sub> need UV illumination. The deposition efficiencies upon separate or mixed  $SiH_4$  and  $O_2$  exposures are similar and depend similarly on the surface stoichiometry. All these results strongly indicate that both photodissociation of molecules into radicals and reaction of these radicals take place at the surface. This is confirmed by a modeling of deposition efficiencies in processes involving various localizations for these reaction steps. This localization of the reaction under the UV beam in low-pressure UVCVD opens perspectives for the direct writing of oxide patterns with a focused UV beam, by avoiding having radicals formed in the gas-phase diffusing out of the beam as in medium-pressure UVCVD and blurring the pattern.

We acknowledge with pleasure fruitful discussions with C. Licoppe and Y. I. Nissim, and technical assistance from F. Barthe.

- <sup>1</sup>L. G. Meiners, J. Vac. Sci. Technol. 21, 665 (1982); K. P. Pande and V. K. R. Nair. J. Appl. Phys. 55, 3109 (1984); B. R. Benett, J. P. Lorenzo, and K. Vaccaro, Electron. Lett. 24, 172 (1988); P. Dimitriou, G. Post, and A. Scavennec, J. Phys. (Paris) C5, 50, 675 (1989).
- <sup>2</sup>Y. I. Nissim, J. L. Regolini, D. Bensahel, and C. Licoppe, Electron. Lett. 24, 488 (1988).
- <sup>3</sup>J. Takahashi and M. Tabe, Jpn. J. Appl. Phys. 24, 274 (1985).
- <sup>4</sup>C. Licoppe, J. M. Moison, Y. I. Nissim. J. L. Regolini, and D. Benshahel, Appl. Phys. Lett. **53**, 1291 (1988); C. Licoppe and J. M. Moison, Surf. Sci. **211/212**, 979 (1989).
- <sup>5</sup>J. M. Moison, Y. I. Nissim, and C. Licoppe, J. Appl. Phys. 66, 3824 (1989).
- <sup>6</sup>F. Houzay and J. M. Moison (unpublished).
- <sup>7</sup>F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J. A. Yarmoff, and G. Hollinger, Phys. Rev. B **38**, 6084 (1988).
- <sup>8</sup>C. D. Wagner, L. E. Davis, M. V. Zeller, J. A. Taylor, R. M. Raymond, and L. H. Gale, Surf. Interf. Anal. 3, 211 (1981); J. J. Scofield, J. Electron Spectrosc. Relt. Phenom. 8, 129 (1976).
- <sup>9</sup>G. Hollinger and F. J. Himpsel, Phy. Rev. B 28, 3651 (1983); F. J. Grunthaner and P. J. Grunthaner, Mater. Sci. Rep. 1, 65 (1986); P. J. Grunthaner, M. H. Hecht, F. J. Grunthaner, and N. M. Johnson, J. Appl. Phys. 61, 629 (1987); M. Nakazawa, S. Kawase, and H. Sekiyama, J. Appl. Phys. 65, 4014 (1989); M. Nakazawa, Y. Nishioka, H. Sekiyama, and S. Kawase, J. Appl. Phys. 65, 4019 (1989).
- <sup>10</sup>G. Hollinger, J. Joseph, Y. Robach, E. Bergignat, B. Commère, P.
- Viktorovitch, and M. Froment, J. Vac. Sci. Technol. B 5, 1108 (1987). <sup>11</sup> B. R. Bennett, J. P. Lorenzo, and K. Vaccaro, Appl. Phys. Lett. 50, 197 (1987).
- <sup>12</sup> Y. Tarui, J. Hidaka, and K. Aota, Jpn. J. Appl. Phys. 23, L827 (1984);
  K. Inoue, M. Michimori, M. Okuyama, and Y. Hamakawa, Jpn. J. Appl. Phys. 26, 805 (1987).
- <sup>13</sup> J. Bénard, editor Adsorption on metal surfaces (Elsevier, New York, 1983).