

Monitoring of III-V semiconductor surface by In-situ Surface PhotoAbsorption

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Abstract

We present the investigation on P- and As-desorption process from the (001) InP surface in metal organic chemical vapor deposition using surface photoabsorption (SPA). The monochromatic SPA signal showed rapid initial increase to reach In-stabilized surface value after PH₃ was turned off, but in case of As-desorption, the signal showed clear existence of a metastable state after the AsH₃ was turned off. The SPA spectra at each stable surfaces were taken to confirm the interpretation. This result indicates that the As-desorption process should be understood as a two-step process, in contrast to P-desorption of one-step process.

Keywords : surface photoabsorption, P-desorption, As-desorption

1. Introduction

In this article, we use surface photoabsorption (SPA) for real time monitoring of P- and As-desorption processes from (001) InP surfaces during metalorganic chemical vapor deposition (MOCVD). MOCVD has been successfully used to grow ultrathin high-quality epilayers for device applications. However, an understanding of growth mechanisms in MOCVD is quite limited since standard electron probes such as reflection high-energy electron diffraction (RHEED) and low-energy electron diffraction (LEED) cannot be used in high pressure MOCVD conditions. Various optical techniques such as surface photoabsorption (SPA) [1], spectroscopic ellipsometry (SE) [2], and reflectance difference spectroscopy (RDS) [3] have emerged to yield information about surfaces during growth. In particular, the SPA has been successfully used to detect monolayer-level reflectivity differences caused by chemical changes in many interesting materials systems [4-6]. From SPA

signal As-desorption process has a metastable state in contrast to one-step of P-desorption.

2. Experiment

Experimental procedures were as follows. After a conventional ex-situ cleaning to remove surface contaminants, the (001) InP substrate was loaded into our horizontal MOCVD reactor. In-situ thermal cleaning was carried out at 620°C for 5 min under a PH₃ atmosphere, followed by deposition of 1000 Å of an InP buffer layer using trimethylindium (TMIn) and PH₃ at 76 Torr. Then, P-adsorption and desorption experiments were performed by switching the PH₃ flow on and off at various temperature. Anisotropic SPA reflectance spectra were taken by directing the incident light along [10] and then [1 $\bar{1}$ 0]. Also, prepared InP buffer layer was lowered to T=470°C under a PH₃ atmosphere to preserve a P-stabilized surface. The PH₃ source was then turned off so that an In-stabilized surface was obtained as the

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starting point. Next, by flowing AsH₃ gas, an As-stabilized surface was obtained. Finally, As was desorbed by closing the AsH₃ supply. Anisotropic SPA reflectance spectra were obtained.

3. Results and Discussion

The SPA responses during P-desorption at various substrate temperature are shown in Fig. 1. The curves were shifted for clarity. It is clearly seen that P desorbs faster from InP substrate as the temperature increases and P-desorption is one-step process. A detail expression of P-desorption has been described elsewhere [7].

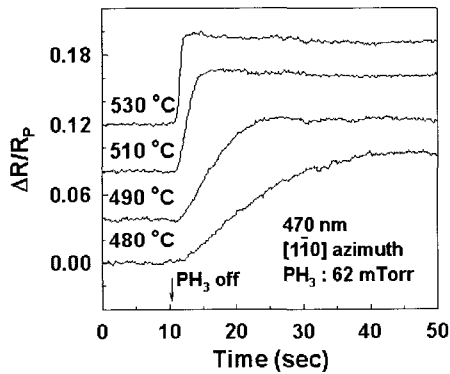


Fig. 1. Change in the SPA signal during P-desorption.

Figure 2(a) shows the SPA signal change at 470 nm when we performed As-adsorption and desorption on (001) InP surface at 470°C with the incident light directed along $[1\bar{1}0]$ and $[110]$. Upper solid lines represent the state of the gas supply, so that high (low) values indicate on (off) state. The SPA signals were normalized by the signal from the P-stabilized surface (R_p) where $\Delta R/R_p = (R - R_p)/R_p$. Note that the curves have been vertically shifted for clarity. The upper signal along $[1\bar{1}0]$ direction shows the same behavior observed in previous reports [6,8] at slightly lower temperature of 400°C in that the SPA signal shows rapid initial increase to reach In-stabilized surface value (In-surface) after PH₃ was turned off, sharp decrease and quick recovery to

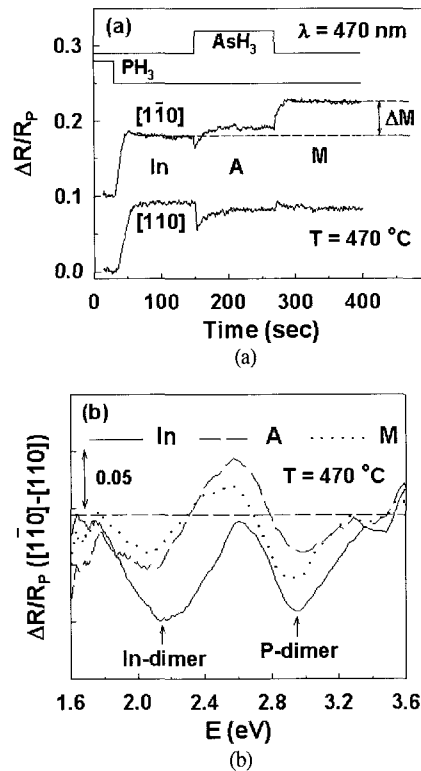


Fig. 2. (a) SPA signal at 470nm during P-desorption, As-adsorption, and As-desorption at 470°C. (b) SPA subtraction spectra for In-, A-, and M-surfaces.

slightly higher value of As-stabilized surface (A-surface) during AsH₃ supply, and a final stable value (M-surface) after AsH₃ was turned off. This final M-surface was interpreted as In-stabilized surface in previous reports [6,8]. The reason why the SPA signal of the same In-stabilized surface before and after AsH₃ supply is different was also interpreted by the formation of 1-2 monolayer thick InAsP layers under the surface caused by As/P exchange reaction. Therefore, the ΔM value in Fig. 2(a) has been used as the measure of the amount of As/P exchange reaction [6,8].

However, when we obtained the SPA signal along $[110]$ direction also shown in Fig. 2(a), the SPA signal showed no specific increase after AsH₃ was turned off. We expected the similar increase because the embedded InAsP layers by As/P exchange may cause isotropic

response in SPA reflectivity. We therefore speculated that this M-surface after AsH_3 was turned off was not the In-surface but an intermediate state.

To verify this interpretation, we obtained SPA subtraction spectra for each of the In-, A-, and M-surfaces of Fig. 2(a). The subtraction equation we used is the conventional formula [8]. It should be noted that the SPA monochromatic signal is not mono-wavelength value of the SPA subtraction spectrum [9]. The resultants are shown in Fig. 2(b) where the solid, dashed, and dotted lines show the SPA spectra for In-, A-, and M-surfaces, respectively. Based on previous works [8,10], two negative peaks near 2.1 eV and 2.9 eV for the In-surface spectrum can be identified as a [110] In-dimer related peak and a [10] P-dimer related peak, respectively, while strong positive peak in the 2.4-2.6 eV region at A- and M-surfaces are interpreted as As-dimer related. The positive value indicates that the direction of the As-dimer is parallel to [10] as same as other group V atom-dimers.

It is clear that the SPA spectrum of M-surface, which was obtained by As-desorption, is not similar to that of the In-stabilized surface. On the contrary the M-surface spectrum is closer to that of the A-surface of the As-stabilized surface, showing clear positive As-dimer peak contribution, which suggests that the change in surface chemistry after As-desorption is not significant. Therefore, our result at $T = 470^\circ\text{C}$ shows that the M-surface after As-desorption cannot be interpreted as an In-surface but an intermediate state.

To achieve the real In-stabilized surface we performed the same experiment at higher temperature of $T = 570^\circ\text{C}$ as shown in Fig. 3(a). It is clear that the M-surface which was a stable state at 470°C is only a transient state at 570°C , quickly evolving to a new stable state (S-surface), indicating that the S-surface may be the real In-surface. Therefore, Fig. 3(a) clearly indicates that the As-desorption from (001) InP surface occurs as a two-step process.

To confirm our analysis, we obtained SPA subtraction spectra for each of the states. The resultants are shown

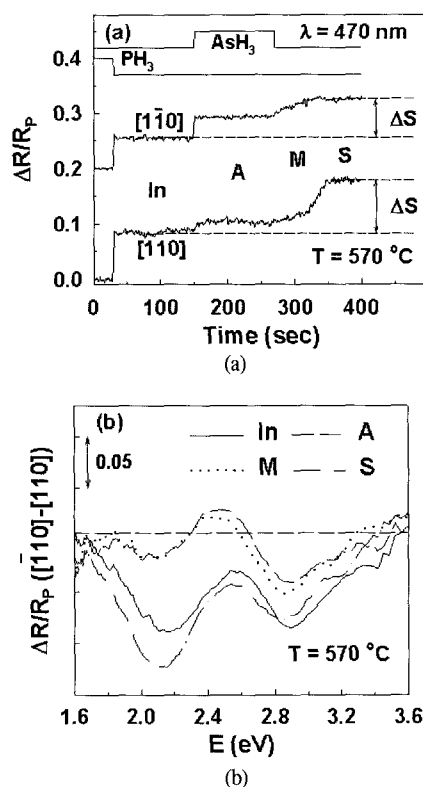


Fig. 3. (a) SPA signal at 470nm during P-desorption, As-adsorption, and As-desorption at 570°C . (b) SPA subtraction spectra for In-, A-, and M-surfaces.

in Fig. 3(b). As was the case of 470°C , the spectrum of M-surface (dotted line) at 570°C is similar to that of A-surface (dashed line), while the spectrum of the final S-surface (dot-dashed line) is close to that of pure In-surface (solid line). Negative values of S-surface spectrum at the 2.4-2.6 eV region means that there is no As-dimer contribution, indicating that As was totally desorbed from the surface to result in In-stabilized surface.

Figure 4 illustrates our interpretation of P- and As-desorption process. During P-desorption process, P-dimers were desorbed to reach In-surface whose dimer direction is perpendicular to the paper. However during As-desorption, the weakly-bonded excess As desorbs from the surface first to reach M-surface of intermediate state. Then, in contrast to P-desorption of a one step

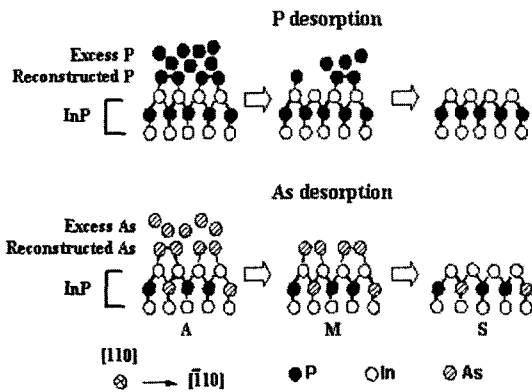


Fig. 4. Illustration of P- and As-desorption mechanism.

process [1,1], we need an extra 2nd process for desorption of chemically-bonded anisotropic As-dimers to reach the pure In-stabilized top surface which has underneath InAsP layer. Therefore, we conclude that the real In-surface is not the M-surface but the S-surface, and that the amount of As/P exchange effect should be analyzed by amount of ΔS value in Fig. 3(a), not by the ΔM value in Fig. 2(a).

4. Conclusions

We have analyzed the surface structures of (001) InP during P- and As- desorption under an MOCVD growth environments using SPA. We observed that the surface after As-desorption is not In-stabilized but is rather in an metastable state. This is different from one-step of P-desorption process. We concluded that there is two-step during As-desorption and the measure of As/P exchange should be determined between the In- and the S-surface.

Acknowledgments

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References

- [1] N. Kobayashi and Y. Kobayashi, *Jpn. J. Appl. Phys.* **30**, L1699 (1991).
- [2] I. Kamiya, D. E. Aspnes, L. T. Florez, and J. P. Harbison, *Phys. Rev. B* **46**, 15894 (1992).
- [3] D. E. Aspnes, J. P. Harbison, A. A. Studna, and L. T. Florez, *Phys. Rev. Lett.* **59**, 1687 (1987).
- [4] N. Kobayashi and Y. Kobayashi, *Thin Solid Films* **225**, 32 (1993).
- [5] Y. D. Kim, F. Nakamura, E. Yoon, and D. V. Forbes, and J. J. Coleman, *Appl. Phys. Lett.* **69**, 4209 (1996).
- [6] N. Kobayashi and Y. Kobayashi, *J. Cryst. Growth* **124**, 525 (1992).
- [7] T.W. Lee, H. Hwang, Y. Moon, E. Yoon, and Y. D. Kim, *J. Vac. Sci. Technol. A* **17**, 2663 (1999).
- [8] N. Kobayashi, *J. Cryst. Growth* **145**, 1 (1994).
- [9] T. W. Lee, H. Hwang, Y. Moon, E. Yoon, and Y. D. Kim, *J. Vac. Sci. Technol. A* **17**, 2663 (1999).
- [10] M. L. Begarney, C. H. Li, D. C. Law, S. B. Visbeck, Y. Sun, and R. F. Hicks, *Appl. Phys. Lett.* **78**, 55 (2001).
- [11] T. W. Lee, H. Hwang, Y. Moon, E. Yoon, and Y. D. Kim, *J. Kor. Phys. Soc.* **34**, S461 (1999).