AIP Applied Physics Letters

As/P exchange on InP(001) studied by reflectance anisotropy spectroscopy

Z. Sobiesierski, D. I. Westwood, P. J. Parbrook, K. B. Ozanyan, M. Hopkinson et al.

Citation: Appl. Phys. Lett. **70**, 1423 (1997); doi: 10.1063/1.118595
View online: http://dx.doi.org/10.1063/1.118595
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v70/i11
Published by the American Institute of Physics.

Related Articles

Pulsed-laser excited thermal lens spectroscopy with sample-fluid heat coupling
J. Appl. Phys. 107, 083512 (2010)

Enhanced absorption of metals over ultrabroad electromagnetic spectrum
Appl. Phys. Lett. 95, 121106 (2009)

Phase change mechanisms during femtosecond laser pulse train ablation of nickel thin films
J. Appl. Phys. 106, 064906 (2009)

Experimental tests of effective mass and atomistic approaches to quantum dot electronic structure: Ordering of electronic states
Appl. Phys. Lett. 94, 243116 (2009)

Optical and ultrasonic signatures of femtosecond pulse filamentation in fused silica
J. Appl. Phys. 105, 123106 (2009)

Additional information on Appl. Phys. Lett.

Journal Homepage: http://apl.aip.org/
Journal Information: http://apl.aip.org/about/about_the_journal
Top downloads: http://apl.aip.org/features/most_downloaded
Information for Authors: http://apl.aip.org/authors

ADVERTISEMENT

ACCELERATE AMBER AND NAMD BY 5X.
TRY IT ON A FREE, REMOTELY-HOSTED CLUSTER.
LEARN MORE

Downloaded 30 Mar 2012 to 131.251.133.25. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions

As/P exchange on InP(001) studied by reflectance anisotropy spectroscopy

Z. Sobiesierski[a] and D. I. Westwood
Department of Physics and Astronomy, University of Wales College Cardiff, Cardiff CF2 3YB, United Kingdom

P. J. Parbrook, K. B. Ozanyan, M. Hopkinson, and C. R. Whitehouse
Department of Electronic and Electrical Engineering, IRC for Semiconductor Materials, University of Sheffield, Sheffield S1 3JD, United Kingdom

(Received 4 November 1996; accepted for publication 10 January 1997)

Reflectance anisotropy spectroscopy (RAS) has been used to investigate the As/P exchange reaction for group V stabilized InP(001) surfaces exposed to As_2 and/or P_2, under molecular beam epitaxy conditions. By comparing RAS spectra taken before, during, and after As_2 exposure it is possible to confirm that the As/P exchange reaction is exactly reversible over a range of temperatures from 420 to 560 °C. Time-resolved RAS measurements of the reaction rate, monitored at an energy of 2.65 eV, indicate that the activation energy for the exchange is 1.23 ± 0.05 eV. © *1997 American Institute of Physics.* [S0003-6951(97)02511-4]

The exchange of group V atoms on the surface of a III–V semiconductor can affect both the interface properties and thickness of quantum structures. In molecular beam epitaxy (MBE), the desorption of the surface oxide from InP substrates is often carried out under a stabilizing As flux in order to avoid the use of phosphorus.[1] Oxide removal under As stabilization of the InP surface results in the exchange of P for As atoms, leading to the formation of a thin pseudomorphic InAs layer on the InP surface.[2,3] The structural properties of such InAs layers have been investigated in some detail,[3] with a consensus being reached that the InAs surface layer invariably stabilizes at around two monolayers thickness, with very little As incorporation beyond the second monolayer from the surface. Moreover, the InAs/InP interface thus formed is of sufficient quality to allow efficient carrier capture and radiative recombination within the InAs/InP surface quantum well.[4] Hence, the exposure of the InP surface to an As flux suggests itself as an appropriate system with which to study the kinetics of the As/P exchange reaction.

In situ optical probes have been used recently to investigate the kinetics of As/P exchange on InP(001),[5] and P/As exchange on GaAs(001),[6] under metalorganic chemical vapor deposition (MOVPE) conditions; as well as As capture by InP(001) surfaces under chemical beam epitaxy conditions.[7] In the first case,[5] surface photoabsorption (SPA) at 470 nm was used to monitor the change in surface reflectivity on exposure of the InP(001) surface to AsH_3. An activation energy of 1.26 eV was obtained for As/P exchange based on various assumptions, including the fact that only a single monolayer is affected by the exchange process. In addition to being limited to a fixed wavelength, it has been noted[6] that this study was performed on the group III terminated (In) surface, a somewhat unusual condition for conventional epitaxial growth. In the second case, reflectance anisotropy spectroscopy (RAS) was used[6] to measure the temperature and pressure dependence of P/As exchange for GaAs(001) exposed to PH_3. In this case, the activation energy for P/As exchange was determined to be 1.64 eV using the time-resolved RAS response at 2.5 eV.

The sensitivity of the RAS technique to both the orientation and type of surface dimer species has been well illustrated by studies of both GaAs(001) surface reconstructions,[8] and the deposition of submonolayer coverages of Si on the GaAs(001)–$c(4\times4)$ surface.[9] Furthermore, the quantitative abilities of RAS have also been demonstrated recently during H desorption studies from vicinal Si(001) surfaces.[10] In this letter we present RAS data for P-stabilized InP(001) surfaces exposed to As. By comparing spectra taken before, during, and after As exposure it is possible to determine the extent to which the As/P exchange reaction is reversible. Also, measuring the time taken for the surface to convert from being P to As terminated upon As exposure, as a function of temperature, allows an activation energy to be extracted for the As/P exchange reaction.

All processes took place on InP(001) on-axis substrates within a VG Semicon V80H MBE reactor. Solid sources were used for In, cracked As (As_2) and cracked P (P_2). The in-house constructed RAS system, based upon a design due to Aspnes *et al.*,[11] was positioned at a strain-free pyrometer viewport situated on the MBE reactor growth chamber. The RAS system, which has a working spectral range from 1.5 to 5.5 eV, measures the difference (Δr) between the anisotropic complex reflectance (r) along the [−110] and [110] crystallographic axes within the (001) surface plane, normalized to the mean reflectance ($\bar{r}$):

$$\frac{\Delta r}{\bar{r}} = 2\frac{r_{[\bar{1}10]} - r_{[110]}}{r_{[\bar{1}10]} + r_{[110]}}.$$

Only the real part of the RAS signal was investigated, since even small residual strain effects, associated with the pyrometer viewport, significantly affect the imaginary component of the RAS signature.

Following thermal desorption of the surface oxide under a P_2 pressure of 3.5×10^{-6} mbar, a 0.5 μm InP buffer was grown at 510 °C. RAS spectra were subsequently acquired for static (i.e., no growth) surfaces before, during, and after As_2 exposure, in the presence of the P_2 flux. RAS transients, monitored at an energy of 2.65 eV (peak energy of a feature

[a]Electronic mail: spxzs1@cf.ac.uk

 © 1997 American Institute of Physics

Downloaded 30 Mar 2012 to 131.251.133.25. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions

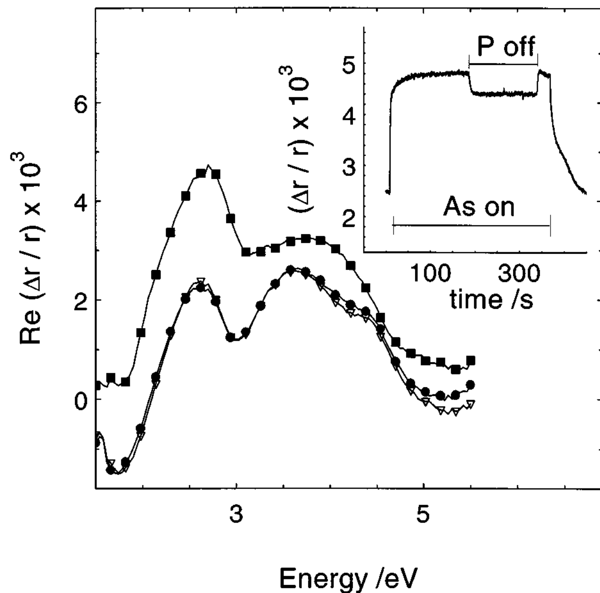

FIG. 1. RAS spectra measured at 510 °C for InP(001) before (●), during (■), and after (▽) exposure to an As_2 flux of 4.6×10^{-6} mbar. The inset shows a time-resolved measurement performed at 2.65 eV during a similar sequence.

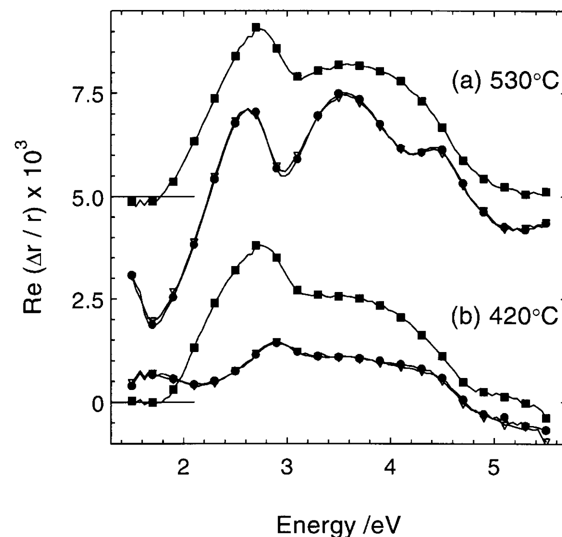

FIG. 2. RAS spectra measured at (a) 530 °C, and (b) 420 °C, for InP(001) before (●), during (■), and after (▽) exposure to As_2 fluxes of 1.2×10^{-5} and 2.8×10^{-6} mbar, respectively. The horizontal lines indicate the corresponding ''zero'' levels for the two sets of spectra.

related to surface As–As bonds) were also recorded during the initial exposure and final removal of the As_2 flux.

Figure 1 displays the RAS spectra obtained at 510 °C before, during, and after exposure of the InP(001) surface to a 4.6×10^{-6} mbar As_2 flux. Sufficient time was allowed (~3 min) for the surface to stabilize, in each case. The peak located at 2.65 eV for the clean InP surface remains at approximately the same energy following As_2 exposure, rather than shifting to 2.3 eV, the energy characteristic of bulk InAs. This behavior is fully consistent with the formation of a very thin InAs layer, pseudomorphically matched to the InP substrate, and similar spectra have also been observed for thin InAs layers (<10 ML) grown on InP(001).[12] The overall similarity in shape between the RAS spectra for the clean, and As-exposed, InP surfaces indicates that the surface symmetry remains essentially unaltered during the exchange process. This observation has been verified by simultaneous RHEED measurements, taken during As_2 exposure, which reveal that the reconstruction is (2×4). By performing separate measurements, using incrementally larger As_2 fluxes, it has been possible to establish that exposure to an As_2 flux of 4.6×10^{-6} mbar provides the greatest change in RAS response, at this temperature. In this respect, it will be referred to subsequently as the ''optimal'' flux.

Since the largest spectral change following As_2 exposure occurs around 2.65 eV, the energy characteristic of surface dimer species, this energy has been used to monitor the temporal behavior during the As/P exchange process. The inset to Fig. 1 shows a time-resolved measurement of the RAS intensity at 2.65 eV before, during, and after As_2 exposure. In addition to the transients obtained at the start and end of As_2 supply to the surface, it can be seen that the signal also decreases when the P_2 flux is turned off. Similar behavior can also be obtained, in the presence of P_2, by increasing the As_2 flux above the ''optimal'' level of 4.6×10^{-6} mbar described previously. This indicates a complicated dependence on the total group V flux, a matter which will be dealt with in more detail elsewhere.[12]

Figure 2 contains similar sequences of spectra obtained at temperatures of (a) 530 °C and (b) 420 °C, with ''optimal'' As_2 fluxes of 1.2×10^{-5} and 2.8×10^{-6} mbar, respectively. The InP(001) reconstruction for the clean, P stabilized surface was found to alter from (2×4) at 530 °C to (2×2) at 420 °C. The data in Fig. 2 show clearly that the As/P exchange reaction is fully reversible over a range of temperatures from 420 to 530 °C. In fact, RAS measurements performed at temperatures as high as 560 °C show a similar degree of reproducibility between the spectrum obtained for the clean InP(001) surface and the spectrum following application and removal of the As_2 flux. However, at this elevated temperature it has not been possible to supply enough As_2 to saturate the spectral change observed for the As-exposed surface. This is probably due to the high evaporation rate for As from the surface at 560 °C.

RAS transients, monitored at an energy of 2.65 eV during As_2 exposure, have been acquired over the entire temperature range studied. The time taken for the change in intensity to reach 95% of its maximum value has been determined, and the reaction rate has been defined as the reciprocal of this quantity. Figure 3 shows an Arrhenius plot of the natural logarithm of the reaction rate versus reciprocal temperature. The activation energy for As/P exchange on InP(001) obtained in this manner is 1.23 ± 0.05 eV. This can be compared directly with a value of 1.26 eV obtained from SPA measurements on the In-rich InP surface, using a much narrower range of temperatures from 370 to 400 °C, under MOVPE conditions.[5]

In conclusion, RAS measurements have been used to investigate the As/P exchange process on InP(001) surfaces exposed to an As_2 flux, under MBE conditions. This system is ideally suited to a study of the As/P exchange process, since it is known to provide a thin overlayer (~2 ML) of InAs on InP. While a previous study[5] using MOVPE condi-

Downloaded 30 Mar 2012 to 131.251.133.25. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions

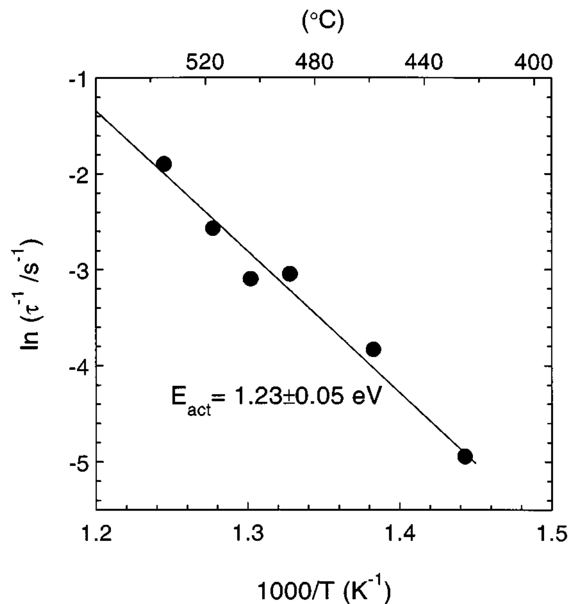

FIG. 3. Natural logarithm of the rate constant for As/P exchange [as determined from the RAS transients on As exposure to InP(001)] vs reciprocal temperature.

tions only measured the reflectivity change during the exchange process at a fixed wavelength, we have been careful to compare the RAS spectra before, during, and after As_2 exposure. In this way, it is possible to confirm that the As/P exchange reaction is exactly reversible over a range of temperatures from 420 to 560 °C, in a MBE environment. RAS transients measured at an energy of 2.65 eV allow an activation energy of 1.23 ± 0.05 eV to be determined for As/P exchange on InP(001) surfaces, under these conditions.

Financial support from the United Kingdom SERC Low Dimensional Structures and Devices Initiative, and the IRC for Semiconductor Materials and EPSRC Central Facility for III–V Semiconductors is gratefully acknowledged.

[1] G. J. Davies, R. Heckingbottom, H. Ohno, C. E. C. Wood, and A. R. Calawa, Appl. Phys. Lett. **37**, 290 (1980).
[2] J. M. Moison, M. Bensoussan, and F. Houzay, Phys. Rev. B **34**, 2018 (1986).
[3] G. Hollinger, D. Gallet, M. Gendry, C. Santinelli, and P. Viktorovitch, J. Vac. Sci. Technol. B **8**, 832 (1990).
[4] Z. Sobiesierski, S. A. Clark, R. H. Williams, A. Tabata, T. Benyattou, G. Guillot, M. Gendry, G. Hollinger, and P. Viktorovitch, Appl. Phys. Lett. **58**, 1863 (1991).
[5] N. Kobayashi and Y. Kobayashi, J. Cryst. Growth **124**, 525 (1992).
[6] J. Jönsson, F. Reinhardt, M. Zorn, K. Ploska, W. Richter, and J. Rumberg, Appl. Phys. Lett. **64**, 1998 (1994).
[7] D. E. Aspnes, M. C. Tamargo, M. J. S. P. Brasil, R. E. Nahory, and S. A. Schwarz, J. Vac. Sci. Technol. A **12**, 1180 (1994).
[8] I. Kamiya, D. E. Aspnes, L. T. Florez, and J. P. Harbison, Phys. Rev. B **46**, 15894 (1992).
[9] D. A. Woolf, K. C. Rose, J. Rumberg, D. I. Westwood, F. Reinhardt, S. J. Morris, W. Richter, and R. H. Williams, Phys. Rev. B **51**, 4691 (1995).
[10] J. Zhang, A. K. Lees, A. G. Taylor, M. H. Xie, D. Raisbeck, B. A. Joyce, Z. Sobiesierski, and D. I. Westwood (unpublished).
[11] D. E. Aspnes, J. P. Harbison, A. A. Studna, and L. T. Florez, J. Vac. Sci. Technol. A **6**, 1327 (1988).
[12] K. B. Ozanyan, P. J. Parbrook, M. Hopkinson, C. R. Whitehouse, Z. Sobiesierski, and D. I. Westwood (unpublished).

Downloaded 30 Mar 2012 to 131.251.133.25. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions