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Photoelectron spectroscopic study of amorphous GaAsN films

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Amorphous gallium–arsenic–nitrogen (*a*-GaAsN) thin films were deposited by sputtering a crystalline GaAs target with different mixtures of argon and nitrogen. X-ray photoelectron spectroscopy (XPS) and x-ray excited Auger electron spectroscopy (XAES) were employed to study the Ga and As core levels and the corresponding LMM Auger transitions of films with different N concentrations. Chemical information of these samples was obtained through the analysis of the Auger parameter, which is exempt from problems inherent in the interpretation of XPS and XAES shifts, revealing aspects associated with the composition of the *a*-GaAsN films. In particular, these experimental results show the preferential bonding of N to Ga atoms in the formation of N-rich amorphous GaAsN films. © 2000 American Institute of Physics. [S0003-6951(00)02816-3]

Recently, there has been a great deal of interest in N-based semiconductor compounds due to their prospective employment in the field of optoelectronics and high-temperature devices.¹ Crystalline (*c*-)GaAs_{1-x}N_x ternary alloys, in particular, have been intensively investigated, anticipating the achievement of N-dependent tunable optical band-gap semiconductors.² Analogously, and of fundamental importance in the manufacture of insulator–semiconductor interfaces with a low density of defects, is the passivation of *c*-GaAs surfaces with N atoms.^{3–5} The attainment of such advantageous optical and electronic properties, however, presents problems such as:^{6–12} a large difference in the lattice constants of the parent GaAs and GaN binaries preventing the continuous variation of their properties, an unusual composition-dependent optical band gap in dilute *c*-GaAs_{1-x}N_x alloys, phase separation at appreciable N concentrations due to low N solubility in the *c*-GaAs_{1-x}N_x alloys, etc. Within certain limits, most of these drawbacks are absent, or can be avoided, in the case of amorphous (*a*-)GaAsN compounds. To that aim, however, an essential stage is the identification and the understanding of the different steps governing the formation of these amorphous films.

In this letter, the experimental report on the photoelectron spectroscopic (PES) properties of *a*-GaAsN films containing different N concentrations is presented. Given the insulating characteristics of these films, the present analysis in terms of the Auger parameter yields a set of data, which is thoroughly unsusceptible to experimental problems associated with the charging effects and energy shifts commonly found in most of the photoelectron spectroscopic studies.¹³

Thin films of *a*-GaAsN were deposited by radio frequency (13.56 MHz) sputtering a *c*-GaAs wafer in a controlled Ar+N₂ atmosphere. Moreover, in order to study the photoluminescent properties of these films, they were doped with Er by putting suitable pieces of metallic Er onto the

c-GaAs target during deposition. Since the Er contained in the samples is at doping levels (~0.5 at. %, as determined from x-ray micro-analysis), the structural properties of the material are not influenced by its presence (see below). Therefore, here we shall focus our attention exclusively on the structural changes introduced by N while the effects of Er on the optical properties of the *a*-GaAsN films are reported elsewhere.¹⁴ All films were grown at room temperature on polished *c*-Si substrates. They are typically ~2 μm thick and exhibit an amorphous structure, as indicated by Raman scattering measurements. All x-ray photoelectron spectroscopy (XPS) measurements were obtained under ultrahigh vacuum conditions (<10⁻⁹ mbar) using a nonmonochromatic Al Kα_{1,2} photon source ($h\nu=1486.6$ eV, full width at half maximum height ~1.2 eV). They were accomplished *ex situ* and no cleaning procedures (either chemical or physical) were performed in order to avoid possible mixing and/or preferential sputtering. As a consequence, the analyzed samples always had a thin superficial naturally grown oxide layer. The binding energy E_B corresponding to Ga 3*d* and As 3*d* core levels were obtained following standard computer data fitting procedures and taking into account bonds with N and O atoms.¹⁵ The data of the $L_3M_{45}M_{45}$ Auger transitions were obtained from the derivative of the photoelectron spectra and expressed in terms of their respective kinetic energy E_k . According to this procedure, the Auger parameter α was determined from $\alpha=E_B+E_k$.¹⁶ As a consequence, α is conceived to be an empirical measure with a unique value for each chemical state and can be used as a “fingerprint” for the identification of such states.^{13,16}

Figure 1 shows the photoelectron spectra of some GaAs(N) samples in the range of ~0–450 eV binding energy. The spectrum of a *c*-GaAs sample, measured under very similar conditions, is also represented for comparison purposes. The main features are identified in the figure and correspond to: [Fig. 1(a)] valence band states and, the Ga 3*d* and As 3*d* core levels; [Fig. 1(b)] the As LMM Auger transitions and the C 1*s* core levels (the latter, most probably stemming from atmospheric exposure); and [Fig. 1(c)] the

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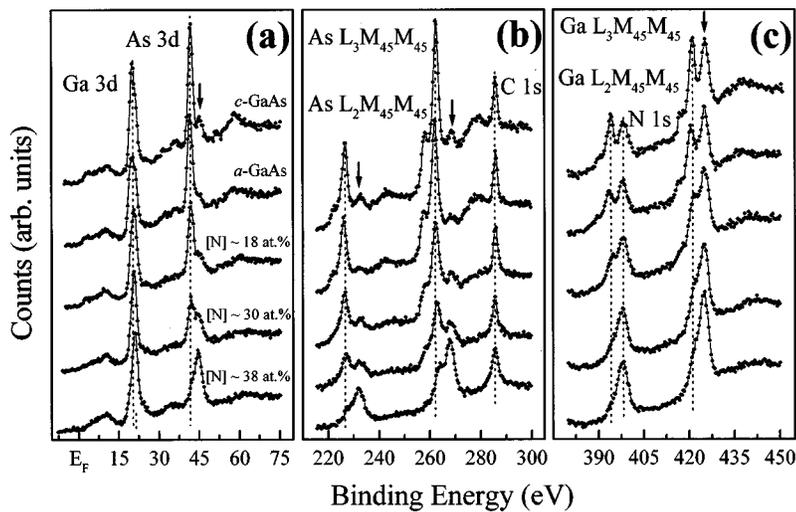


FIG. 1. X-ray photoelectron spectra (XPS) in the binding energy range of ~ 0 –450 eV of some GaAs(N) compounds. The following electron transitions can be specified: (a) valence band states (up to 15 eV), Ga 3*d* and As 3*d* core levels; (b) As LMM Auger transitions and C 1*s* core levels and; (c) Ga LMM Auger transitions and N 1*s* core level. *c*-GaAs (*a*-GaAs) stands for a commercial wafer of crystalline GaAs (pure amorphous GaAs film). The nitrogen content of the *a*-GaAsN films, as estimated from the XPS analysis, were indicated in (a). The most evident O-related bonds are identified by downward arrows in the figure.

Ga LMM Auger transitions and the N 1*s* core levels. As a consequence of the thin oxide layer on the surface of all samples, O-related bonds¹³ are evident from the spectra (Fig. 1).

The spectra of Fig. 1(a) suggest the preferential bonding of O to the As atoms. Also, it is important to notice the changes experienced by the As 3*d* core levels and As-related LMM Auger transitions at increasing N contents [N]. The same is true for the As 3*p* and 3*s* core levels (not shown). Based on the atomic concentration of Ga, As, and N, most of these features are attributed to the replacement of As by N atoms.

Concerning the behavior exhibited by the Ga-related core levels, increasing amounts of N are responsible for a small energy shift of the Ga 3*d* core levels and a new bonding arrangement [Fig. 1(a)]. Both the energy shift and the appearance of a new chemical environment indicate the development of Ga–N bonds. As recently reported,¹⁴ the formation of these Ga–N bonds is responsible for the development of new electronic states at the top of the valence band [Fig. 1(a)] and the widening of the optical band gap from ~ 1.5 to 2.5 eV in the *a*-GaAsN films.

Figure 2 illustrates the Auger parameter α of the *a*-GaAs(N) films as a function of [N]. For the purpose of comparison, the α of *c*-GaAs, GaN, GaO_{*n*}, and AsO_{*n*} compounds are also included.¹³ The N content of the *a*-GaAsN films was determined from the XPS data and, as expected, scales with the N₂ partial pressure adopted during deposition.¹⁴ The overlapping of the N 1*s* core level with the Ga L₂M₄₅M₄₅ Auger transition [Fig. 1(c)] introduces inaccuracies in the estimation of the N content that is indicated in Fig. 2. Also displayed in Fig. 2 are the error bars associated with the experimental determination of the Auger parameter of all *a*-GaAs(N) samples.

Regarding the experimental data represented in Fig. 2, some important conclusions follow:

(a) Despite some data dispersion, the α values associated with the As atoms remain almost the same for all [N], implying a chemical environment constituted essentially by As–Ga bonds [Fig. 2(a)].

(b) On the other hand, for [N] ≥ 30 at. % the Ga-related Auger parameter indicates a systematic change towards the α value characteristic of the GaN system [Fig. 2(b)].

(c) For $10 < [N] < 25$ at. %, the Auger parameters are very similar to those representative of As–As [Fig. 2(a)] and Ga–Ga [Fig. 2(b)] bonds, suggesting some metallic-like character in these films. In other words, intermediate amounts of N promote the development of Ga–Ga and As–As bonds in the *a*-GaAsN system. Indeed, this could be the origin of the optical band-gap decrease proposed for *c*-GaAs_{1–*x*}N_{*x*} compounds in the $0 < [N] \leq 25$ at. % range.^{2,6,11}

Finally, it is important to stress that the α values of all *a*-GaAs films are not influenced by the presence of Er (see the experimental values corresponding to [N]=0 at. % in Fig. 2). Furthermore, in view of the typical α values designating GaO_{*n*} and AsO_{*n*} environments¹³ the data corresponding to the present *a*-GaAsN system are clearly not affected

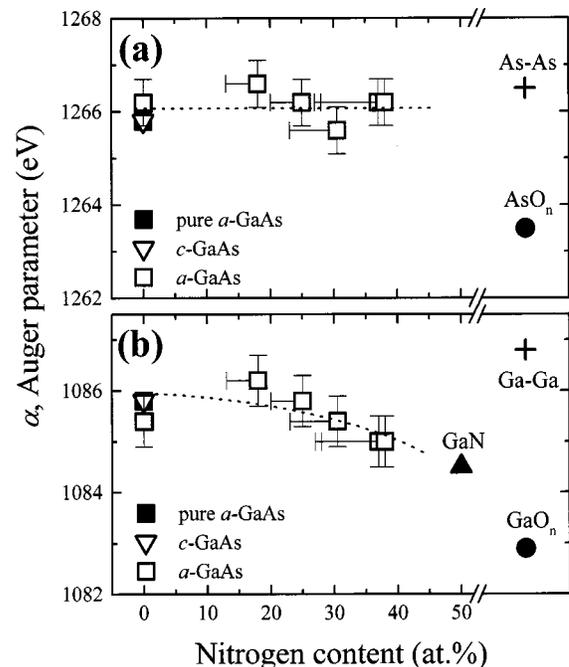


FIG. 2. As- and Ga-related Auger parameters of a series of *a*-GaAs(N) films with different concentrations of nitrogen [N]. The Auger parameter of *c*-GaAs, pure *a*-GaAs, metallic As and Ga, AsO_{*n*}, GaN, and GaO_{*n*} are also represented for comparison (see Ref. 13). The lines are guides to the eyes. The error bars indicate both the experimental resolution of the Auger parameter and the uncertainties in the estimation of [N].

by the *ex situ* analysis (Fig. 2). Conversely, with the actual experimental information, the surface structure formed by atmospheric exposure is more difficult to elucidate. As remarked above, it seems that As atoms are more susceptible than Ga to form chemical bonds with O since the Ga 3*d* core level is indifferent to the O presence [Fig. 1(a)]. On the other hand, the trend of α towards the expected value of the GaN compound is strong evidence of the preferential bonding of N to Ga. Therefore, all changes verified in the Ga-related *LMM* Auger transitions [Fig. 1(c)] result either from an increase in the number of N atoms ($L_2M_{45}M_{45}$ transition) or from the energy shift due to the formation of Ga–N bonds ($L_3M_{45}M_{45}$ transition). If it is so, the energy shift in the As core levels must be due to As–Ga–N bonds [Figs. 1(a) and 1(b)]. However, since some features associated with O and N are overlapping, it is not possible to exclude completely the existence of a small number of As–N bonds [see, for example, the data corresponding to $[N] \sim 30$ at. % in Fig. 2(a)].

The data displayed in Fig. 2 shows that *a*-GaAsN compounds can have their N composition continuously varied in the $0 < [N] < 40$ at. % range. Therefore, besides their possible usage as insulating layers in GaAs-based devices, the growth of *a*-GaAsN samples with well defined and controlled amounts of N represents a suitable choice for applications that demand compounds with tunable optical band gaps.² Moreover, in analogy with amorphous Si- and Ge-based alloys, it is expected that the optical and electronic properties of *a*-GaAsN could be further improved (or changed) with the insertion of hydrogen atoms. Finally, under specific deposition conditions, it is possible to easily achieve stoichiometric *a*-GaN, which is promising as a novel electronic material.¹⁷

Summarizing, in this letter we presented a PES study of amorphous GaAsN films, deposited by rf sputtering a *c*-GaAs wafer under different partial pressures of N₂. Both x-ray photoelectron spectroscopy (XPS) and x-ray excited

Auger spectroscopy (XAES) data were employed to determine the Auger parameter α of a series of samples with different N content. In contrast to previous efforts aimed at understanding GaAsN compounds, the present analysis based on α is free from charging problems inherent in the interpretation of XPS and XAES spectra of insulating films. The analysis of this parameter allows us to draw conclusions about the preferential bonding of N to the Ga atoms in the formation of N-rich *a*-GaAsN films.

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- ¹H. Morkoç, S. Strike, G. B. Gao, M. E. Lin, B. Sverdlov, and M. Burns, *J. Appl. Phys.* **76**, 1363 (1994).
- ²G. Pozina, I. Ivanov, B. Monemar, J. V. Thordson, and T. G. Andersson, *J. Appl. Phys.* **84**, 3830 (1998).
- ³C. R. Brundle and D. Seybold, *J. Vac. Sci. Technol.* **16**, 1186 (1979).
- ⁴S. Gourrier, L. Smit, P. Friedel, and P. K. Larsen, *J. Appl. Phys.* **54**, 3993 (1983).
- ⁵I. Aksenov, Y. Nakada, and H. Okumura, *J. Appl. Phys.* **84**, 3159 (1998).
- ⁶W. G. Bi and C. W. Tu, *Appl. Phys. Lett.* **70**, 1608 (1997).
- ⁷A. Ougazzaden, Y. LeBellego, E. V. K. Rao, M. Juhel, L. Leprince, and G. Patriache, *Appl. Phys. Lett.* **70**, 2861 (1998).
- ⁸Y. Qiu, S. A. Nikishin, H. Temkin, V. A. Elyukhin, and Y. A. Kudriavtsev, *Appl. Phys. Lett.* **70**, 2831 (1997).
- ⁹E. V. K. Rao, A. Ougazzaden, Y. LeBellego, and M. Juhel, *Appl. Phys. Lett.* **72**, 1409 (1998).
- ¹⁰S. Francouer, G. Sivaraman, Y. Qiu, S. Nikishin, and H. Temkin, *Appl. Phys. Lett.* **72**, 1857 (1998).
- ¹¹W. K. Hung, M. Y. Chern, J. C. Fan, T. Y. Lin, and Y. F. Chen, *Appl. Phys. Lett.* **74**, 3851 (1999).
- ¹²J. D. Perkins, A. Mascarenhas, Y. Zhang, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, *Phys. Rev. Lett.* **82**, 3312 (1999).
- ¹³*Practical Surface Analysis* 2nd ed., Auger and X-ray Photoelectron Spectroscopy, Vol. 1, edited by D. Briggs and M. P. Seah (Wiley, New York, 1990), and references therein.
- ¹⁴A. R. Zanatta, *Appl. Phys. Lett.* **75**, 3279 (1999).
- ¹⁵See, for example, A. R. Zanatta, R. Landers, S. Castro, G. G. Kleiman, I. Chambouleyron, and M. L. Grilli, *Appl. Phys. Lett.* **66**, 1258 (1995).
- ¹⁶C. D. Wagner, *Discuss. Chem. Soc.* **60**, 291 (1975).
- ¹⁷P. Stumm and D. A. Drabold, *Phys. Rev. Lett.* **79**, 677 (1997).