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S. R. McHale

J. W. McClory

J. C. Petrosky

J. Wu

R. Palai

See next page for additional authors

Authors
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S.R. McHale [a,*], J.W. McClory [a,**], J.C. Petrosky [a], J. Wu [b], R. Palai [b,c], P.A. Dowben [c], I. Ketsman [c]

[a] Air Force Institute of Technology, 2950 Hobson Way, Wright Patterson Air Force Base, OH 45433, USA
[b] Department of Physics and Institute for Functional Nanomaterials, University of Puerto Rico, Río Piedras, Natural Sciences Building, Phase II, San Juan, Puerto Rico, 00931, USA
[c] Department of Physics and Astronomy, Nebraska Center for Materials and Nanoscience, University of Nebraska, P.O. Box 880111, Lincoln, NE 68588–0111, USA

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ABSTRACT

The effective Debye temperature of ytterbium and gallium in Yb:GaN thin films has been obtained using X-ray photoemission spectroscopy. The vibrational motion normal to the surface results in a dimunition of photoemission intensities from which we have estimated the effective Debye temperatures of 221 ± 30 K and 308 ± 30 K for Yb and Ga, respectively. The difference between the measured values for Yb and Ga suggests that the Debye temperatures are influenced by the local environment. The smaller effective surface Debye temperature for Yb correlates to a soft, strained surface, possibly due to an increased Yb—N bond length as compared to the Ga—N bond length.

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1. Introduction

During the past decade, rare-earth doped semiconductors have generated considerable attention for their application in new optoelectronic devices [1–4]. The favorable thermal, chemical, and electronic properties of wide band gap, III-nitride semiconductors suggest device feasibility using lanthanide-doped AlN and GaN. Moreover, the tunable band gaps of these III-nitride alloys offer device applications across the visible spectrum through the ultraviolet range, to include optically stimulated lasers [5], *p-n* junction light emitting diodes [6], and thin film electroluminescence of phosphors [7–9].

Phonon mediated exciton decay can lead to line broadening and spectral deformation. While phonons can affect excited state lifetimes, so too can the carrier concentration and local structural deformation. A signature of phonon mediated processes would be a low effective Debye temperature. The true surface Debye temperature, containing the in-plane and anharmonic motions, is difficult to measure in most surface spectroscopies [10]. However, the effective surface Debye temperature is readily obtained using X-ray photoemission spectroscopy (XPS) and ultraviolet photoemission, low energy electron diffraction, inverse photoemission spectroscopy, and other surface sensitive techniques [11–21]. The experimentally derived effective surface Debye temperature is dominated by the dynamic motion of vibrational modes normal to the surface and tends to be independent of surface orientation [10,18]. Increased thermal vibrations dictate that the intensity of an emitted or scattered electron beam decays exponentially with increasing temperature as [11–21]

$$I = I_0\, exp(-2W), \tag{1}$$

where W is the Debye–Waller factor and is given by

$$2W = |\Delta k|^2 \langle u_0 \rangle^2, \tag{2}$$

where Δk is the wave vector transfer and $\langle u_0 \rangle^2$ is the mean square displacement of the atoms. Within the Debye model of thermal vibrations, in the case of isotropic vibrations, W is described as

$$2W = \frac{3\hbar^2(\Delta k)^2 T}{m k_B \Theta_D^2}, \tag{3}$$

where $\hbar(\Delta k)$ is the electron momentum transfer, T is the temperature of the sample (in Kelvin), m is the mass of the scattering center, k_B is the Boltzmann constant, and Θ_D is the effective surface Debye temperature. In the case of photoemission spectroscopy, the momentum transfer is equal to the momentum of the emitted electron [11–21], and the scattering center mass is the mass of the specific element from which the emitted photoelectron originates [16]. This paper reports the effective surface Debye temperatures of Ga and Yb via XPS spectra taken from Yb:GaN thin films and correlates the results with thin film strain.

2. Experimental

Thin films of $Yb_xGa_{1-x}N$ (50–300 nm) were fabricated on Si(111) substrates by RF plasma (EPI 620) assisted molecular beam epitaxy (MBE). The growth parameters for the deposition of Yb-doped (in situ) GaN thin films were base pressure of $\sim 10^{-11}$ Torr, nitrogen flux

* Principal corresponding author.
** Corresponding author.
E-mail addresses: stephen.mchale@afit.edu (S.R. McHale), john.mcclory@afit.edu (J.W. McClory).

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of 0.75–1.0 SCCM, RF power of 500 W, substrate temperature of 850–900 °C, Ga cell temperature of 850 °C, and Yb cell temperature of 500–850 °C. Thickness of the films was measured with a surface profile meter. The orientation, crystal structure, and phase purity of the films were established by Cu K_α ($\lambda = 1.5406$ Å) radiation X-ray diffraction, as shown in Fig. 1, using a Siemens D5000 X-ray diffractometer.

Surface adsorbates were removed by several preparatory sputtering and thermal annealing cycles in ultra high vacuum (UHV). The resulting surfaces were characterized by core level XPS and found to be free of oxygen. The XPS studies were performed in an UHV chamber with a hemispherical electron analyzer (Thermo VG Scientific VG100AX). The combined resolution of the system was about 1.1 eV using a Mg K_α line (1253.6 eV) from a fixed anode X-ray source. Surface temperature was controlled by a combination of resistive heating and cooling with liquid nitrogen. The temperature was monitored with a W-5%Re/W-26%Re thermocouple with an accuracy of 5 K. The photoemission spectra were taken with a 45° incidence angle and normal emission, with binding energies referenced to the Fermi level of a clean Ta foil.

3. Results and discussion

As anticipated, the core level photoemission intensities decrease with increasing temperature, as shown in Fig. 2(a) and (b). Fig. 3 shows the logarithm of the core peak photoemission intensities for Ga 3*p* and Yb 4*d* as a function of temperature. The kinetic energy of the outgoing photoelectron is calculated as

$$E_{kin} = h\nu - |E_B| - \phi_a, \tag{4}$$

where $h\nu$ is the incident photon energy, $|E_B|$ is the binding energy of the emitted photoelectron, and ϕ_a is the electron analyzer work function (4.5 eV). Thus, Δk values in Fig. 3 are calculated from

$$(\Delta k)^2 = \frac{2m_e E_{kin}}{\hbar^2}, \tag{5}$$

where m_e is the electron mass. From (1) and (3), the slope S for each XPS data set in Fig. 3 determines Θ_D from

$$|S| = \frac{3\hbar^2(\Delta k)^2}{mk_B\Theta_D^2}. \tag{6}$$

The fact that the effective Debye temperature is different for ytterbium and gallium in a Yb:GaN thin film indicates that this

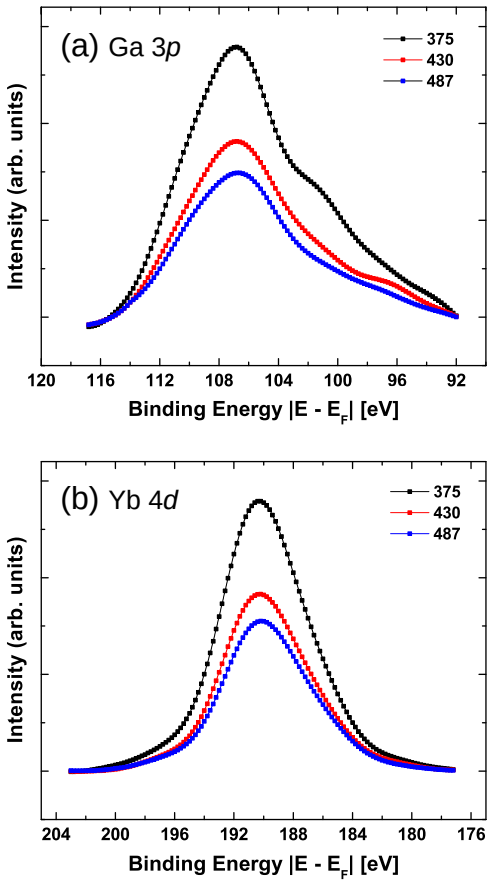

Fig. 2. Temperature dependent X-ray photoemission spectra of the indicated core levels after background subtraction.

effective Debye temperature is influenced by the local environment, not exclusively by the overall rigidity of the thin film lattice. The difference between the measured effective Debye temperatures for Ga and Yb provides an indication of the surface rigidity and lattice strain. In a simple picture, the examination of Eqs. (2) and (3) predicts an inverse relationship between atomic displacement and surface Debye temperature such that an increased Θ_D predicts lower atomic displacement, or a "rigid" surface. It follows that a decreased Θ_D is indicative of a "soft" surface. Thus, our respective values of 221 ± 30 K

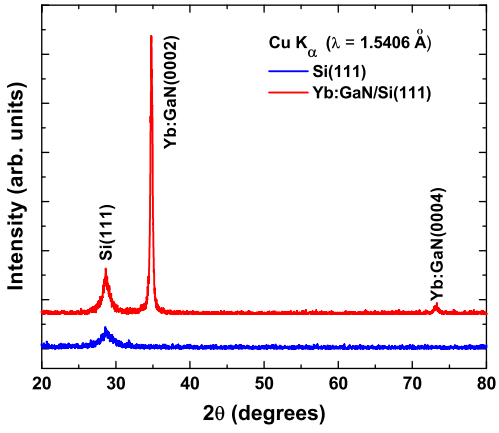

Fig. 1. The X-ray diffraction (XRD) pattern of a Yb:GaN film grown on Si(111) substrates. The films show c-axis orientation of the texture growth and a high level of crystallinity. The presence of any secondary phases or spurious peaks has not been observed.

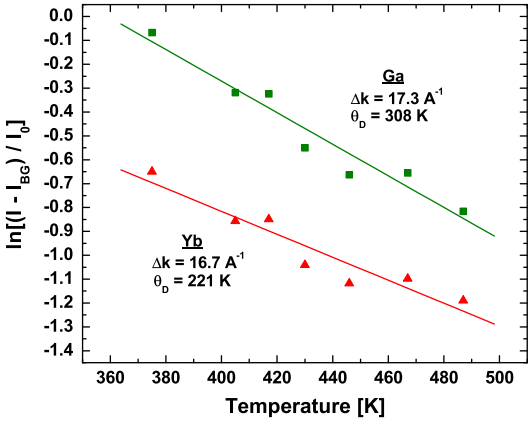

Fig. 3. Logarithm of the core peak photoemission intensities for Yb and Ga as a function of temperature following background (I_{BG}) subtraction and normalization to the peak intensity at the lowest temperature I_0. The experimental values were fitted (solid line) with the Debye–Waller factor.

and 308 ± 30 K for the effective Yb and Ga Debye temperatures in the Yb:GaN thin film reflects softening from the introduction of Yb atoms into the GaN wurtzite crystal structure.

If our measured effective Debye temperatures for Yb and Ga were identical, within experimental uncertainty, it would be indicative of a substitutional occupation of a Ga site by a Yb ion. Although the measured effective Debye temperatures were not identical, the experimental uncertainty indicates that the Yb and Ga Debye temperatures could differ by as little as 27 K. This similarity between the Yb and Ga Debye temperatures suggests that Yb doping does occur by Ga site substitution. Experimental data and crystal-field calculations have confirmed that rare-earth ions in a GaN host occupy relaxed substitutional Ga sites [1,2]. To explain the slight difference in the Debye temperatures, strain should be considered. From the standpoint of bond length, shorter bonds have higher binding energies than longer ones, which implies that decreasing the bond distance reflects stiffening and increasing bond distance reflects softening. Thus, the slightly lower calculated effective Debye temperature for Yb in Yb:GaN reveals a softened surface, and we contend that this softening arises from a lengthening of the Yb—N bond distance, as compared with the Ga—N distance, which would manifest as thin film strain. The decrease in Debye temperature should be reflected in a decrease in exciton lifetime as this means that new phonon decay channels are opened. This in turn should lead to an increase in fluorescence peak widths.

From Fig. 1, the c-axis length of our Yb:GaN thin films was found to be approximately 5.172 Å, which is slightly larger than the widely reported and accepted c-axis length of undoped GaN (5.166 Å). The XRD data are limited because the films are so very nearly crystalline, that is to say highly textured. There will be changes to the a- and b-axis lengths in response to contraction or transverse strain, as dictated by Poisson's ratio. However, the implementation of Poisson's ratio depends on the details of the stress–strain tensor, which cannot be determined accurately from our experimental data. Thus, the values for the a-axis and b-axis cannot be accurately established from our data, but would require additional measurements like grazing incidence X-ray scattering. However, the small increase in c-axis lattice constant, and hence thin film strain, can be explained due to the fact that the Yb^{3+} (8.7 Å) ion has a larger ionic radius than the Ga^{3+} (6.2 Å) ion. This observation suggests the substitutional doping of Yb ions at Ga sites, and further supports the claim of doping-induced thin film strain due to increased Yb—N bond length, compared with the Ga—N bond length.

4. Conclusions

X-ray photoemission spectroscopy has been used to determine the effective Debye temperatures of gallium and ytterbium in Yb:GaN thin films. The similarity between their measured values suggests that substitutional occupation of a Ga site by a Yb ion occurs, which supports experimental data and theoretical calculations. Careful comparison of the Ga and Yb values indicates that the slightly smaller effective Debye temperature of the Yb atom reflects a surface that is softened and strained, possibly due to an increased Yb—N bond length as compared to the Ga—N bond length.

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