Morphological, optical, and photoluminescent characteristics of $GaAs_{1-x}N_x$ nanowhiskered thin films

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(Received 29 May 2001; accepted for publication 9 August 2001)

$GaAs_{1-x}N_x$ solid-solution thin films of nanometric size were prepared on glass substrates by the radio-frequency sputtering technique. Atomic-force microscopy images show that the films are composed of grains with a whisker shape, whose size is practically independent of the substrate temperature. Their typical diameters range between 40 and 45 Å. The surface morphology exhibits a high density of whisker-like features that are almost normal to the substrate plane. This density increases as the substrate temperature increases, but, in essence, the nanowhisker diameter does not. Optical absorption spectra of the samples show a band-gap energy blueshift as large as 1.5 eV with respect to that of the GaAs bulk value, which was associated with strong quantum-confinement effects. Photoluminescence emission spectra in the blue range of 428–438 nm confirm the quantum-size effects in the $GaAs_{1-x}N_x$ nanowhiskered thin films. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1412283]

Research on quantum-wire and quantum-dot structures has been motivated largely by the promise of these structures for improved optoelectronic devices.[1–3] Several experimental attempts to fabricate quantum wires, using both nanofabrication techniques and crystal growth methods, have been reported.[4–6] If the control in the growth of ultrafine wire-like grains in semiconducting thin films were possible, it could lead to physical phenomena and devices based on quasi-one-dimensional carrier transport in ultrafine wires. $GaAs_{1-x}N_x$ is an attractive material from which one can expect excellent quantum-confinement effects which would shift the band-gap energy (E_g) into the blue spectral region. Preparation of GaAsN superlattices has already been reported.

$GaAs_{1-x}N_x$ nanowhiskered thin films were grown on glass substrates employing a rf magnetron sputtering system with a water-cooled cathode. A GaAs (100) high-quality wafer was used as the anode. Different samples (eight) were prepared at substrate temperatures (T_s) in the range from room temperature (RT) to 400 °C (20, 100, 150,..., 350, 400 °C), with a constant growth time of 120 min, a working 100% ultrapurity nitrogen gas at 10 mTorr, and a rf power of 100 W. The crystalline structure and average diameter size of the nanowhiskers were obtained from x-ray diffraction (XRD) patterns (not shown here), using a Siemens D5000 diffractometer (Cu $K\alpha$ radiation) and a crystal size software program.[7] The average particle size was estimated to be around 40 ± 10 Å in diameter. Measurements of stoichiometry were carried out through energy-dispersive spectroscopy (EDS) and wavelength-dispersive spectroscopy (WDS), and the x values measured were in the range 0.0055–0.0085.

Atomic-force microscopy (AFM) pictures show the fibronic nature of the grains in the $GaAs_{1-x}N_x$ films. Figure 1(a) displays a representative image of the surface morphology at the early stage of growth after 10 min of deposition time at RT. We can observe features suggestive of incipient whisker formation growing on the glass surface, with nucleation centers randomly distributed and agglomerates with low packing density. Small islands also show clearly the needle-like grains. Figures 1(b), 1(c), and 1(d) display AFM images of GaAsN films deposited at RT and 100 and 300 °C, with a constant deposition time of 120 min. Figure 1(b) ex-

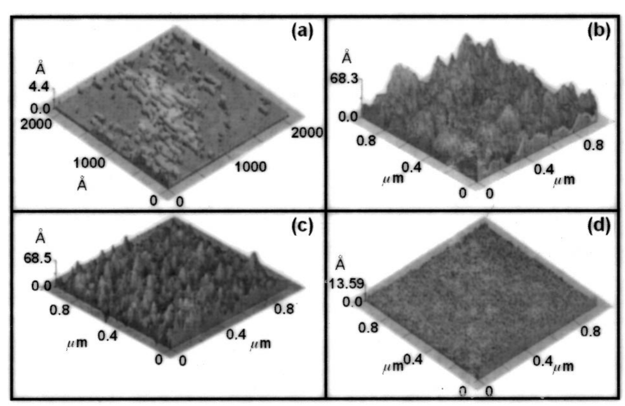

FIG. 1. (a) AFM image of the growth start of nanowhiskers. Deposition time = 10 min at T_s = RT; (b), (c), and (d) are typical AFM images of $GaAs_{1-x}N_x$ nanowhiskered films, prepared at T_s = RT and 100 and 300 °C, respectively, with a deposition time of 120 min.

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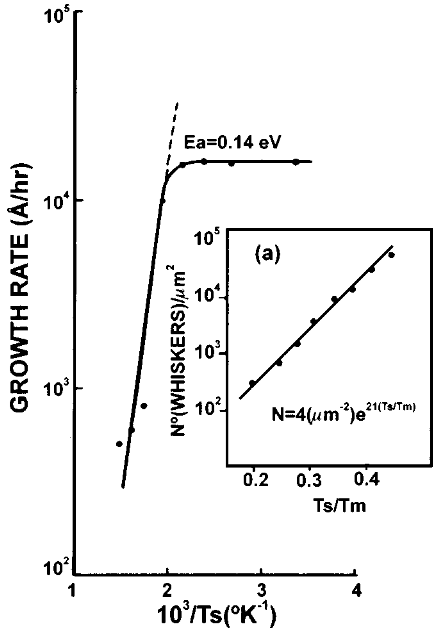

FIG. 2. Growth rate for $GaAs_{1-x}N_x$ nanowhiskered thin films, deposited by rf sputtering as a function of T_s. The activation energy for the condensation process is 0.14 eV. The inset shows the behavior of N with respect to T_s. T_m is the melting point of bulk GaAs.

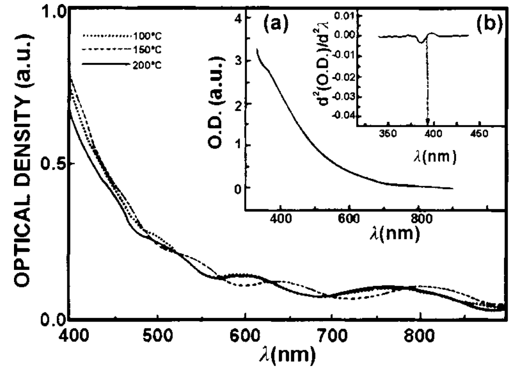

FIG. 3. Absorption spectra of three representative samples. Inset (a) illustrates a typical smoothing spectrum. Inset (b) displays the zero value of the second derivative position which points out the E_g value in the photon wavelength axis.

hibits a nonhomogeneous surface morphology, constituted by bunches of whiskers with different average heights and cross sections which originate from a relative high surface roughness.[7] The diameter of the whiskers is normally measured at the middle point of the full length for each whisker.[8] In our case, the diameter of the whiskers was measured by the AFM technique, i.e., only the upper top can be measured since the cantilever cannot penetrate deep into the surface sample without producing damage. The whiskers shown in Fig. 1(b) have a typical surface diameter ranging between 40 and 45 Å. Figure 1(c) shows a high density of whiskers with more uniform agglomerates and with smaller average cross sections. Grains grow almost normal to the substrate surface, with practically the same grain diameter as the whiskers grown at RT. In Fig. 1(d) a smoother surface can be observed densely populated with whiskers, but without observable aggregates. It can be seen that the number of whiskers per square micrometer (N) increases drastically as T_s increases.

The growth rate as a function of T_s was determined from the film thickness measured on the different samples using a profilometer with a spatial resolution of about 1%. The films were masked and steps were made by chemical etching in the noncovered regions with a $H_2O_2+H_2SO_4$ solution. Figure 2 illustrates the data of the growth behavior for GaAsN films, showing a thermally activated growth process as expected from the basic theory of nucleation on solid surfaces; the process has an activation energy of 0.14 eV for this growth mechanism.[9] In the inset of Fig. 2, the behavior of N as a function of T_s is shown. It is clear that the increase in whisker density is due to an increase in nucleation sites on the substrate surface. However, the growth rate for the sample at RT has a value of 3 Å/s, which means a whisker height of about 1800 Å after a 10 min deposition time. From the analysis of the AFM image of Fig. 1(a), it is clear that the heights of the needle-like grains and agglomerates are no larger than 5 Å. This result implies that a random element exists in the growth-starting time (unknown) that influences the surface nucleation sites, inducing a delayed time (incubation time) of whisker growth. Experimental studies on the vapor–liquid–solid (VLS) model of whisker growth[10–12] have revealed that impurities can influence this type of growth, sometimes even decisively, and can drastically decrease the growth rate of whiskers.[12] In particular, for GaAs whisker growth, an excess of Ga could act as a liquid-forming impurity.[10]

In our case, the nitrogen gas is a necessary presence for the growth of nanowhiskers, because if GaAs thin films are grown in an argon atmosphere, the grains grow in globular form and not as filaments. This result is indicative that nitrogen is an important element in the growth of nanowhiskers, this could be due to the N ionic species present in the growth plasma which produce Ga–N and As–N species that interact with the surface substrate originating the activation of nucleation sites, with the consequent needle-like grain growth following the VLS process in a similar way to the growth of ITO whiskers reported by Yumoto *et al.*[13]

The optical absorption spectra of three representative samples are depicted in Fig. 3. Maxima and minima in absorption curves denote relatively even layer surfaces. The inset (a) of Fig. 3 shows an averaged spectral curve of a typical sample. The oscillations were eliminated by smoothing the absorption line shape. The second derivative of this last curve is displayed in inset (b) of Fig. 3; the place where the plot of the second derivative versus λ equals zero indicates with good approximation the band-gap-energy value (E_g), as was reported by Hirasawa *et al.* for GaAs nanocrystals embedded in SiO_2.[14] The value of λ in inset (b) is close to 400 nm, which indicates a significant blueshift of E_g compared to the value for bulk GaAs. The increase in the band-gap-energy (ΔE_g) values, owed to quantum-confinement effects, range between 1.37 and 1.57 eV. It is well known that for low values of x ($\leqslant 0.01$) in bulk $GaAs_{1-x}N_x$ solid solutions, E_g decreases when nitrogen concentration increases.[14] In our case, the x-value measurements range between 0.0055 and 0.0085 indicating E_g values of about 1.3–1.4 eV for bulk $GaAs_{1-x}N_x$, as reported in Ref. 15. Nevertheless, the quantum-confinement phenomenon in the nanowhiskers dominates, leading to an increase in this effective E_g value.

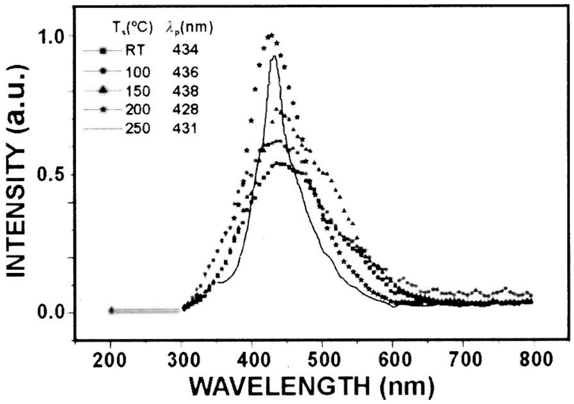

FIG. 4. Photoluminescence spectra of films grown at five different T_s values. λ_p indicates the position where each band peaks.

The photoluminescence of a GaAs bulk crystal is dominated at low temperatures by an excitonic line close to 867 nm. In Fig. 4 are shown the corresponding emission spectra of the $GaAs_{1-x}N_x$ whisker samples excited by a Xe lamp and measured at RT. The emission spectra of these films peaks in the region of 428–438 nm, in agreement with the absorption spectra. By assuming that the maximum emission could provide a good estimation of the energy level of the lowest-excited quantum-confined state, an estimation of the E_g blueshift can be inferred from their emission spectra. Therefore, these samples show a blueshift in E_g in the range $1.40 \leqslant \Delta E_g \leqslant 1.47$ eV at RT. Based on these values, the corresponding average size of the $GaAs_{1-x}N_x$ nanowhiskers can be calculated from an expression reported in Ref. 14, if one assumes spherical particles and the effective masses for electrons and holes in GaAs. The calculated diameter values range from 41.7 to 42.7 Å from the photoluminescence data. From the shifts in the absorption spectra the diameter values range from 40.3 to 46.7 Å. These values match very well with the diameter values obtained from x-ray diffractograms and from AFM images, which were in the interval of 40–45 Å.

In summary, we have reported the growth of $GaAs_{1-x}N_x$ whiskers of nanometric dimensions on glass substrates by the rf magnetron sputtering technique. Crystalline grains of these dimensions for the $GaAs_{1-x}N_x$ ternary compound are reported. It has been found that the average whisker size is independent of the substrate temperature. Meanwhile, the number of whiskers per unit area increases exponentially on T_s. Optical absorption spectra show a drastic blueshift as large as 1.5 eV due to strong quantum-size confinement effects. Photoluminescence measurements indicate a spectral blue emission ($E_g = 2.86 \pm 0.08$ eV) whose intensity increases with the density of whiskers, i.e., with the film growth substrate temperature.

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