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Nanostructured GaAs(N) Thin Films Prepared by RF Sputtering

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An rf sputtering system with a GaAs target was used to grow GaAs(N) nanostructured thin films, on 7059 Corning glass substrates in a N_2 ambient at 10 mTorr, during 120 min. Different substrate temperatures (T_s) were used in the range from room temperature to 400 °C. By Auger spectroscopy it was only possible to determine that the nitrogen content is about 1 at.%. Atomic force microscopy allowed to resolve a well defined fibrous-nature of films, i.e., the grains have the aspect of whiskers. X-ray diffraction patterns were employed to calculate the average grain size of whiskers that was in the range 4.0 to 5.5 nm. The average grain size of whiskers does not change by increasing T_s, however, the density of whiskers increases with T_s following the relationship $\exp[-a(T/T_m)]$, where T_m is the melting point of GaAs and a is a fitting parameter. The growth process is in agreement with the predictions reported by other authors.

Introduction Quantum wires are being studied because of their potential applications in electronic and optical devices. Growth of nanowhiskers is important for fabrication of quantum wire devices [1]. Many works have recently been reported on GaNAs films prepared by molecular beam epitaxy (MBE) technique [2 to 5], however nanostructured films of this ternary compound are still not reported. Nanowhiskers have been obtained in GaAs, InAs, GaAlAs and other III–V semiconductor compounds [3, 6 to 9], however GaNAs nanowhiskers have not been reported until now.

In the present work, as the first step toward the goal of controlling nanowire-like thin film growth, the fabrication of $GaN_{1-x}As_x$ nanowhiskers, with x in the order of 0.01, prepared by rf magnetron sputtering technique on glass substrates is reported. By changing the x parameter from 0 to 1, one could cover a broad energy range between 0 and 3.5 eV, useful for a large variety of light emitting devices [6].

Experimental The GaNAs nanowhisker thin films were grown in an rf magnetron sputtering system, using a water-cooled cathode with a commercial GaAs monocrystalline (110) wafer as target. Different samples (eight) were grown at substrate temperatures (T_s) in the range of room temperature (RT) to 400 °C (RT, 100, 150, 200, 250, 300, 350 and 400 °C), with a constant growing time of 120 min, and maintaining a growth rf power of 100 W with an ultra-purity nitrogen gas pressure of 10 mTorr. The

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samples can be identified as G1 to G8, while T_s going from RT to 400 °C. Sample thickness was measured using a Dektak Sloan profile analyzer. The thickness varied from 2.2 μm for T_s at RT down to 1.0 μm at 400 °C. The growth rate decreased, as expected in rf sputtering deposition processes [9], from 3.05 to 1.94 Å/s [10]. Crystalline structure and average whisker size were obtained from X-ray diffraction (XRD) patterns employing an X-ray Siemens D5000 diffractometer (CuK_α line) and a crystal-size software program, making correction due to equipment intrinsic width-line. Surface morphology, density and average size of whiskers were analyzed by using atomic force microscopy images (Park Scientific Instruments). For the atomic concentration of elements in the layers, Auger and electron dispersion spectroscopy (EDS) measurements were done in a Phi560/Esca-Sam and a Noran Instrument EDS system, respectively. Optical absorption spectra were recorded in a Unicam 8700 UV/VIS spectrophotometer. Luminescence emission was carried out at RT in a Spex-Fluoromax spectrofluorimeter using an excitation wavelength of 300 nm.

Results and Discussion XRD patterns of the eight samples are shown in Fig. 1, where a considerable broadening due to the nanometric dimensions of grains can be observed. The central peak of the broad band is allocated at $2\theta \approx 27.5°$, corresponding to the most abundant (111) planes of crystalline GaAs. Using the Debye-Scherrer formula for the line broadening fitting curve program, the GaN_xAs_{1-x} particle size was estimated in all the samples, the average diameter (calculated as if grains were spheres) were in the interval 40 to 50 Å, after correction owing to intrinsic diffractometer error. A close microstructure view was obtained by atomic force microscopy. The film surface shows a well resolved fibrous structure, which is normally termed whisker-structure. For the concentration x of N, from Auger and EDS techniques it was only possible to know that it is of the order of 1%. Figure 2 shows the EDS spectra of a) a GaAs single-crystal and b) a typical GaN_xAs_{1-x} film. For example, in the case of this layer: Ga = 47.77%, As = 51.23% and N = 1.00% in a first run; Ga = 50.12%, As = 49.03% and N = 0.85% in a second run. More exact measurements of x are under way in order to control the N content in the films.

Figures 3a and b display AFM images of two representative films. One can realize how on the surface of films the whis-

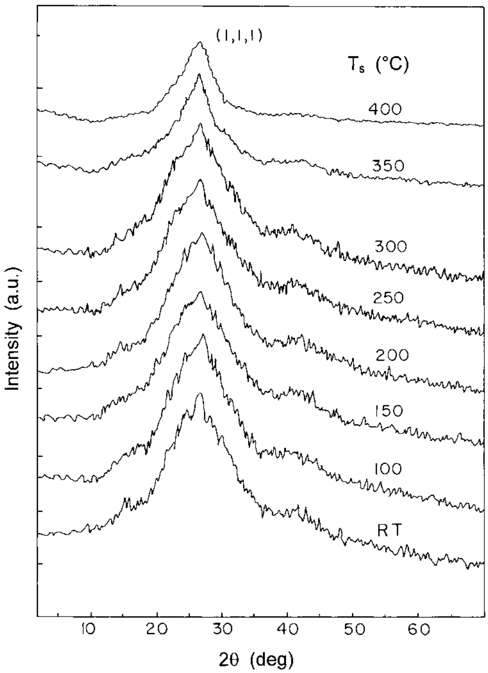

Fig. 1. X-ray diffraction patterns of the eight films grown at different substrate temperatures

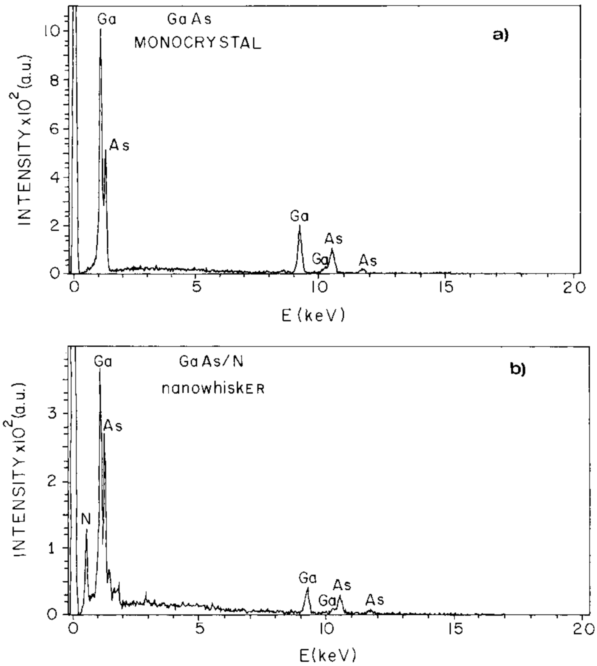

Fig. 2. Electron dispersion spectra of a) GaAs single crystal and b) GaNAs nanowhisker films. The spectrum of nanowhiskers evidences the presence of N in addition to Ga and As

ker density increases as T_s increases. These whiskers grow almost normal to the substrate surface. It is well known [11] that microstructure is a very sensitive property of the deposition conditions. In magnetron sputtering the deposition process depends strongly on the T_s/T_m ratio (here, T_m is the melting point temperature of the deposited material). Figure 4 evidences the functional dependence of the number of whiskers per micron square (N) with the T_s/T_m ratio. Clearly, N increases drastically as T_s/T_m increases, preserving more or less the same average grain size. As T_s increases the height of whiskers becomes more uniform, as it is illustrated in the insets a) and b) of Fig. 5, which also evidence how the average penetration of cantilever diminishes when the

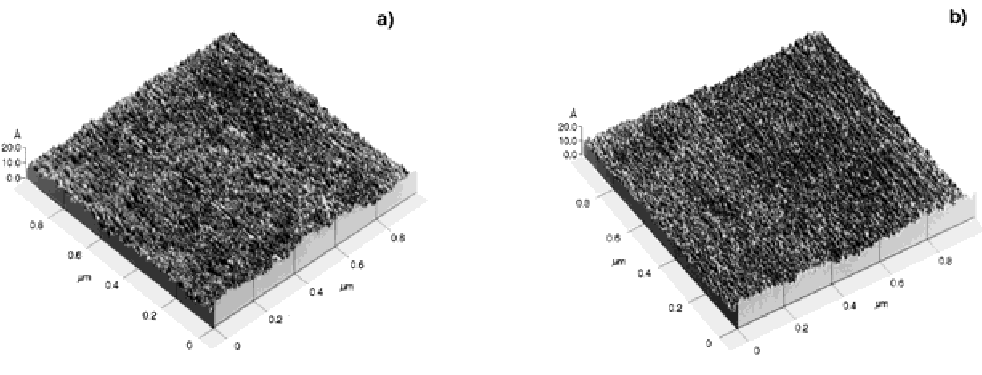

Fig. 3. AFM images of two typical GaNAs films grown at different substrate temperature (T_s): a) 150 ºC, b) 350 ºC

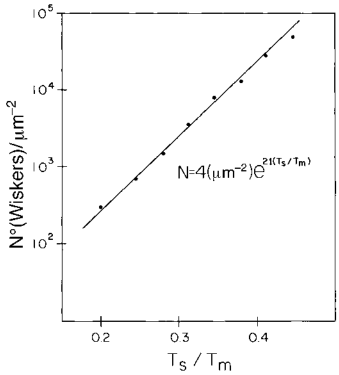

Fig. 4. Logarithm of the number of whiskers per square micron versus the ratio of the substrate temperature (T_s) and the GaAs melting point temperature (T_m)

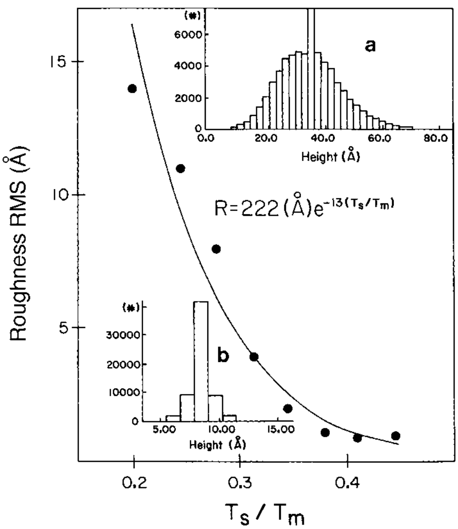

Fig. 5. Root mean square (RMS) of the roughness of the films as a function of the ratio of substrate temperature to GaAs melting point temperature (T_s/T_m). The insets show the nanowhisker-height distribution for samples with a) T_s = RT and b) T_s = 350 °C

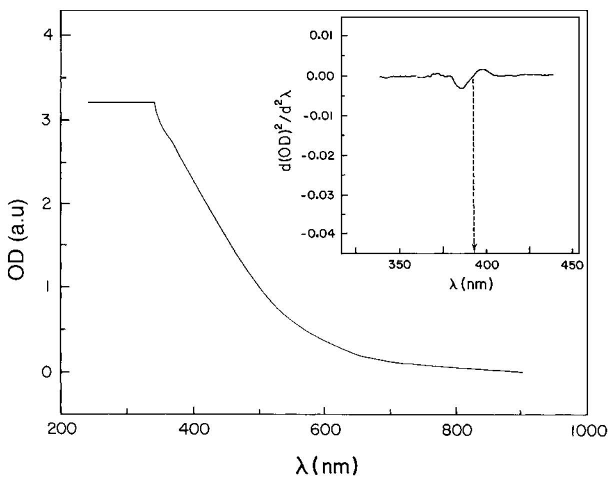

Fig. 6. Typical optical absorption spectrum of GaNAs nanowhisker films. The inset illustrates the position where the second derivative of the optical density (OD) becomes zero, which can be identified with the band gap position

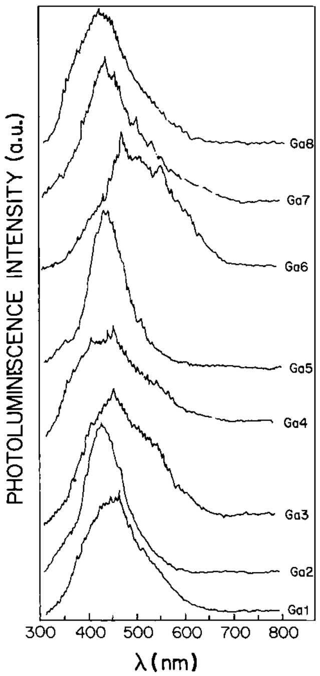

Fig. 7. Photoluminescence signal of the eight GaNAs films. For Ga1, T_s = RT, and so on up to T_s = 400 °C for Ga8

density of whiskers in the films increases. This fact indicates that the root mean square (RMS) of the roughness of the surface of films should diminish when T_s increases. Figure 5 displays an exponential decay of RMS with T_s/T_m. The fitting parameters 4 and 222 and 21 and −13 in the exponential factors, appearing in the functional expressions of Figs. 4 and 5, respectively, depend on the thermal expansion coefficient of material, the substrate temperature, the growing gas pressure, the activation energy for self-diffusion, among others, and their theoretical prediction is not a feasible task [11]. In this work they appear only as numerical fitting parameters. A more complete characterization of the grain size and morphology of growth is in progress and will be published elsewhere.

A typical optical absorption spectrum of the films is shown in Fig. 6; for the energy band gap (E_g) determination the second derivative of the optical density versus the wavelength of incident photon energy was employed [12]. The inset of Fig. 6 illustrates how the E_g value is found. The E_g values determined for all samples (465 ± 25 nm or 2.67 ± 0.14 eV) are significantly blue shift from the bulk absorption edge (867 nm, 1.43 eV). Obviously, this enlargement in E_g is originated by the quantum confinement of charge carriers in the nanowhiskers. This E_g shift to higher energies is confirmed by photoluminescence measurements. Spectra of films as function of the wavelength emission, displayed in Fig. 7, evidence how broad bands peaked in the range 425 nm (2.92 eV) to 514 nm (2.41 eV) for all the samples studied.

Conclusions Summarizing, GaN_xAs_{1-x} nanostructured layers have been reported for the first time. The films were prepared by rf sputtering technique, using N_2 as working-gas and a commercial monocrystalline wafer of GaAs as target. The films grow with grains of whisker structure having nanometric dimensions (40 to 50 Å of average diameter). AFM images evidence the whisker-nature of the layers, and how the numerical density of whiskers increases as the substrate temperature increases. The growth process depends on the ratio of substrate temperature to melting point of the material as described by Thornton and Hoffman [11]. Optical absorption and photoluminescence evidence energy band gap (E_g) values in the range 2.41 to 2.92 eV. The significant E_g blue shift is owing to the quantum confinement of the charge carriers in the GaNAs nanowhiskers.

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