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Section 13. Wide band gap materials. I. Nitride-based alloys

SEM and Raman studies of annealed nanocrystalline GaN and amorphous GaN:O

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Abstract

We report annealing studies of thin films of GaN and GaN:O prepared by ion assisted deposition. As-prepared films of stoichiometric tetrahedrally bonded GaN form nanocrystalline networks, but amorphous networks result with the inclusion of more than 10 at.% of oxygen. The annealed nc-GaN films show an increased average crystallite size, though even after a 700 °C anneal the crystals are no larger than about 10 nm. Annealed a-GaN:O films remain amorphous even after a 700 °C anneal, after which they display a weak photoluminescence.

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1. Introduction

The strong ionicity of GaN has encouraged the suggestion that even in its amorphous form this material may contain so few homopolar bonds as to leave the gap relatively free of localized states, and that it might form a useful electro-optic material [1]. We have investigated the formation of a-GaN by ion assisted deposition (IAD) and found that only by using ion energies of several hundred eV could Ga-rich films be avoided [2]. However, our fully stoichiometric GaN is not amorphous; rather it is nanocrystalline, consisting of random-stacked planes in 'crystals' of typically 3 nm diameter [3]. We attribute this failure to form a-GaN, in contrast with the ease with which a-Si is formed, to the instability of odd-membered rings in a network based on heteropolar-bonded III–V compounds. Imperfect stoichiometry, on the other hand, permits the formation of a random covalent network. In particular we have demonstrated that the introduction of 15% O stabilizes the amorphous phase [3].

There is a potential that either nc-GaN or a-GaN:O films may show useful optoelectronic properties. Optical spectroscopy has demonstrated that nc-GaN has a gap very close to that of crystalline GaN, severely broadened and with a high density of in-gap states. a-GaN:O, in contrast, has a very much reduced level of in-gap states and a somewhat wider gap [4]. Thus there is a clear possibility to tune these important parameters by careful control of the stoichiometry of Ga oxynitride films. For example their photoconductive responses are much weaker in the visible than in the UV, so that they form solar-blind UV detectors. The very much smaller in-gap state density of

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the oxynitrides leads to a photoconductive response that is orders of magnitude stronger than in nc-GaN, and in these we have managed a UV NEP as low as 10^{-8} W/Hz$^{1/2}$ in a photoresistor configuration [4].

In this paper we report our studies of the annealing behavior of the nc-GaN and a-GaN:O films, studying the thermally-driven reconstruction and growth of crystallite, and seeking bonding configurations that might further enhance the exploitable optoelectronic properties. Here we focus on characterization of the annealed films by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Raman spectroscopy and photoluminescence. Raman spectroscopy in particular has been developed as a clear and easily-performed indicator of the degree of short- and intermediate-range order in these films which has encouraged us to use it for monitoring annealing developments [5].

2. Experimental details

The films were formed by depositing Ga atoms at a rate of about 0.1 nm/s while bathing the substrate in 500 eV ions from a Kaufmann-type source at a flux 2–4 times larger than the Ga atom flux. Oxynitride films were grown by introducing water vapor in the chamber at a pressure of 10^{-7} to 10^{-6} mb [3]. The films consist of predominantly tetrahedrally (sp^3) bonded Ga and N atoms, with oxygen substituted for N in a-GaN:O. In all of the films there are N_2 molecules that we believe to be trapped in interstitial positions, and their density is enhanced when O is present [6].

The annealing studies on both stoichiometric and oxynitride films were accomplished in a number of different systems. The most extensive were performed in the SEM environmental chamber at the SCM-U, Provence, Marseille. This system allows a continuous monitoring of the films by SEM during the anneal procedure and thus the selection of the most appropriate thermal regimes. The samples were set in the heating holder of the microscope, under up to 3 torr N_2, in a dynamic regime. Temperature was raised up to 700 °C in four steps, at a rate of 30 °C/min each and with plateaus of 10 min at 450, 500, 650, 700 °C. Cooling down happened at about 5 °C/min. Further studies were performed using this thermal regime with an annealing furnace, under a dynamic pressure of nitrogen. A EUROTHERM controller has been used to achieve the steps already defined in the SEM experiment.

Following annealing the samples were investigated by Raman spectroscopy performed on a Jobin–Yvon LabRam HR microscope spectrometer, fitted with excitation sources across the visible (Ar^+ and HeNe lasers) and at 325 nm in the UV (HeCd laser). The spatial resolution of this instrument permits to focus measurements from a spot of about 1 μm with visible light, and about twice that diameter at 325 nm. As reported earlier the films show resonant Raman enhancement in the UV, and we limit the present Raman reports to that excitation. The films' photoluminescence was measured using the same Raman spectrometer, with both UV and visible excitation. All of the spectra displayed here were collected with the films at ambient temperature.

3. Results

XRD patterns of annealed nc-GaN films show a general growth in the crystallite size, rising to no more than 10 nm after an hour at a temperature of 700 °C. That development is corroborated by the UV (325 nm) Raman data in Fig. 1. In as-prepared films there is a line centered on 720 cm^{-1}, with a width of 50 cm^{-1} suggesting disorder over length scales of more than about 1 nm. We have earlier established that loss of intermediate-range order in the 3 nm crystallites as arising from random-stacking [6]. It is notable that the data of Fig. 1 show both a hardening to 730 cm^{-1}, more typical of the wurtzite phase (w-GaN) [7], and a reduced width of about 30 cm^{-1} consistent with full crystalline order extending out to lengths of 3–5 nm [5]. Thus it is clear that annealing encourages a healing of the stacking faults in addition to the moderate growth of the crystallites signaled by XRD. There is also a strongly increased Raman cross section of the 730 cm^{-1} line after annealing, as would be expected for the enhanced resonance resulting from a steeper optical inter-band onset. Note in that regard that the 325 nm excitation is very close to the center of the inter-band absorption edge [5].

Fig. 2 displays Raman spectra from an as-prepared and annealed amorphous oxynitride film. Although the behavior is qualitatively similar to that in nc-GaN, the post-annealed spectrum remains broad (60 cm^{-1}). It is not clear to what extent the width results from O-related disorder; more detailed annealing/XRD studies are required to characterize the bonding structure in these films fully.

The line centered at 2330 cm^{-1}, which arises from trapped molecular nitrogen [5], is not present after

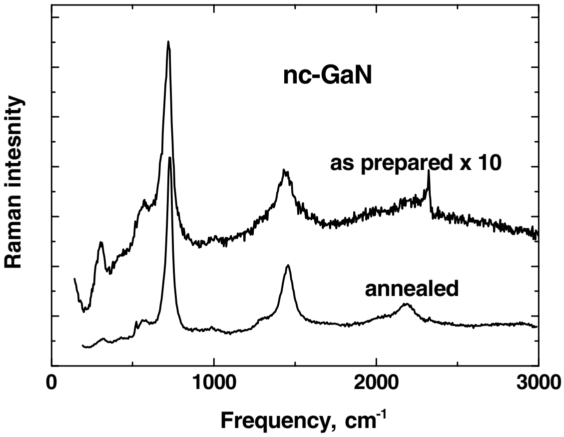

Fig. 1. Raman spectra of a nc-GaN film as prepared and after annealing at 700 °C. After annealing the spectrum is stronger, the prominent peaks narrow and harden, and the N_2 signature is lost.

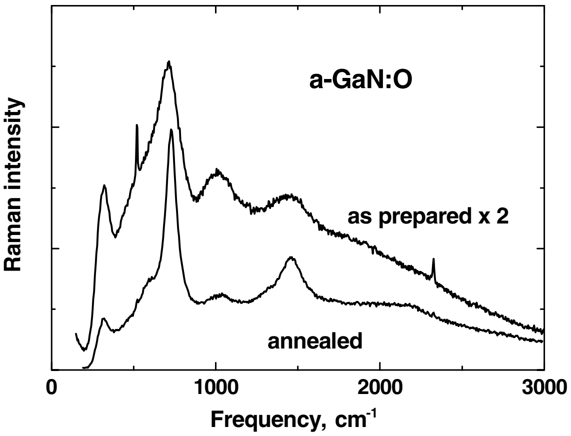

Fig. 2. Raman spectra of an a-GaN:O film as prepared and after annealing at 700 °C. After annealing the spectrum is marginally stronger and the prominent peaks narrow but do not harden significantly.

annealing in either the stoichiometric or the oxynitride films. Clearly the trapped N_2 is released during annealing. In contrast the broad feature O-related centered at $1000\ \text{cm}^{-1}$ [5] is also reduced, though not fully eliminated, by annealing.

Although there is no band-edge luminescence in any of these films, there is a weak red photoluminescence (Fig. 3) in annealed oxynitride films. It is not found in as-prepared or annealed stoichiometric GaN. The PL spectra are very broad, with a peak near 1.6 eV, near the mid-gap energy. It is worth noting in this regard that we have already shown that our oxynitride films have a substantial reduced density of states in the gap, which then reduces non-radiative electron–hole recombination [4]. In contrast the lack of luminescence in our nc-GaN films are a result of their large mid-gap density of states, permitting non-radiative recombination by way of electrons cascading through those states.

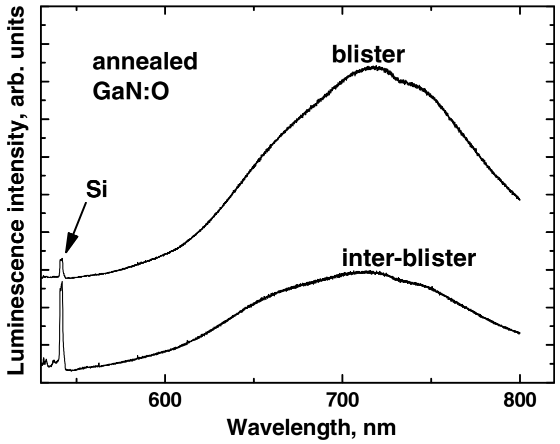

Fig. 3. Luminescence spectrum of an annealed a-GaN:O film excited by 514.5 nm from an Ar^+ laser. The features labeled 'Si' are Raman signals from the substrates. The luminescence is stronger and the Si Raman signal from the substrate weaker on the blisters than on the intact film between the blisters.

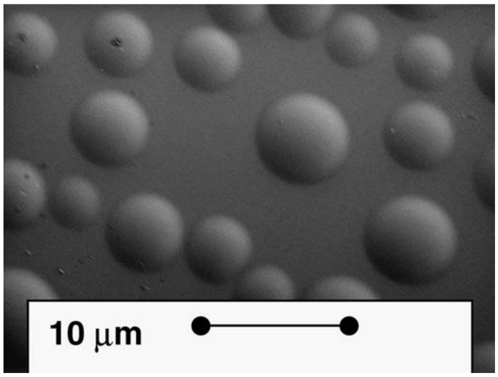

Fig. 4. SEM image of blisters raised after annealing an a-GaN:O film on Si.

We turn next to the morphology of films annealed in the environmental SEM. At 650 °C we observed blisters forming all over the surface of the oxynitride films, which defines the new morphology of those samples. At the conclusion of the procedure it was found that only the films deposited on Si showed a regular distribution of raised blisters (Fig. 4), with a spacing and diameter that appear to scale with the thickness of the film. The similarity to discs reported many years ago in annealed a-Si:H films is striking [8], and their formation is surely very closely related, for in both systems there is trapped gas within the films. It is, however, unclear why then the blisters in our study appear only on films deposited on Si substrates, though that suggests poor bonding, thermal expansion mismatch or even the well-documented release of O from the oxidized surface of Si at elevated temperature. Indeed these may all play a role. Our approximate determination of the density of N_2 in the films places it at somewhat larger than the density of N_2 in air [6], so its release would provide more than enough gas to fill the blisters and raise them to a height of a micron. However, it is notable that the release of N_2 from nc-GaN films leads to no such blistering.

4. Conclusions

The annealing characteristics of initially nanocrystalline GaN have been investigated up to an annealing temperature of 700 °C. The procedure both grows the crystallites and heals stacking faults toward the wurtzite phase. The same procedure applied to amorphous GaN containing 15 at.% of O relaxes strain in the material, as signaled by a narrowing of the most prominent resonant Raman peaks, but the material remains in the amorphous phase. The amorphous oxynitrides display a weak photoluminescence after annealing.

Blisters develop in the a-GaN:O films on Si during annealing, and these display a stronger photoluminescence than is found in between the blisters. Raman spectra suggest that these films lose both O and trapped molecular nitrogen present in the as-prepared films, and it is speculated that these are the gasses that fill the blisters.

Acknowledgements

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