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Low-temperature epitaxial growth and photoluminescence characterization of GaN

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Epitaxial layers of GaN on sapphire substrates have been grown by metalorganic chemical-vapor deposition at a deposition temperature as low as 400 °C, which is the lowest temperature for successful epitaxial growth of GaN by any technique. This is achieved by controlling the low flow rate of the source gases and by first depositing an AlN buffer layer at 400 °C. Low-temperature photoluminescence measurements have been employed to study the optical properties of the films deposited at different temperatures. © 1994 American Institute of Physics.

Recently, the group-III nitride wide band-gap semiconductors and their alloys have been studied intensively^{1–5} for applications in two areas: (1) optical devices, including blue-green light emitting diodes (LED), ultraviolet laser diodes, and ultraviolet detectors, and (2) electronic devices, including devices operating at high temperature, high frequency, and high power, combined with high resistance to radiation damage, and charge storage device applications. Based on their physical properties, novel devices with operating characteristics greatly superior to those made from either silicon or gallium arsenide are conceivable. GaN and AlN form a continuous alloy system whose direct band gap ranges from 3.4 to 6.2 eV, because of which their applications for many novel optical devices including light emitting diodes⁴ and diode lasers are particularly promising. Additionally, the lattice constants of GaN and AlN are similar to 6H-SiC which has recently become commercially available to be used as a substrate.

In the past several years, renewed interest in the group-III nitrides has led to much improvement in the epitaxial film growth techniques for these materials. Epitaxial thin films have been prepared by several methods including chemical-vapor deposition (CVD), metalorganic CVD (MOCVD), and molecular-beam epitaxy (MBE). However, most of these are high-temperature growth techniques, which may introduce contamination from their high-temperature components. For example, typical reported deposition temperatures necessary for successful epitaxial growth of GaN on sapphire by MOCVD have been 900–950 °C. There have been efforts to grow GaN at lower temperatures, such as by plasma-assisted MBE, but there is a problem of trade-off between growth rate and ion damage associated with such techniques.⁵ More knowledge concerning different approaches of low-temperature crystal growth are needed at this stage. Fundamental physical properties of this class of materials will also have to be thoroughly determined in order to evaluate their true potential for novel device applications.

In this letter, we report low-temperature growth of GaN films by MOCVD and their subsequent characterization by x-ray diffraction (XRD) and photoluminescence measurements. We found that epitaxial growth of GaN on sapphire

substrates can be achieved at a deposition temperature as low as 400 °C by controlling the flow rate of the source gases at a low level and by first depositing a thin buffer layer of AlN of about 500 Å at 400 °C. Low-temperature photoluminescence (PL) measurements indicate that the quality of the crystals depends strongly on the growth temperature.

The films were deposited in a horizontal, atmospheric pressure MOCVD reactor. Triethylgallium (TEG), trimethylaluminum, and NH₃ were used as the source gases (all with the purity greater than 99.999%) and He was the carrier gases. The total gas flow rate was about 1000 sccm with 10–30 μmol/min TEG and 20 000 μmol/min NH₃. By first depositing a thin buffer layer of AlN of about 500 Å at 400 °C, epitaxial growth of GaN was obtained at a temperature as low as 500 °C on (0001) sapphire substrates. Figure 1 presents the XRD patterns for GaN films deposited on (0001) sapphire substrates at (a) 400, (b) 500, and (c) 550 °C, and also on a (100) silicon substrate at 550 °C. A single diffraction peak from GaN on sapphire at 34.6° was observed and its intensity increased significantly as the deposition temperature was increased from 400 to 500 °C. However, no further change in structural properties was observed as the deposition temperature was increased further, e.g., to 550 °C as shown in Fig. 1(c). The results shown in Fig. 1 indicate that epitaxial films were obtained even at 400 °C, which is the lowest temperature for epitaxial growth of GaN among all techniques. Additionally, the diffraction pattern produced by a Reed thin-film camera also verifies that the films deposited above 500 °C were epitaxial. The crystal-growth process at such low temperatures was attributed primarily to heterogeneous reactions.⁶ Similar investigations were carried out by using (100) and (111) silicon as substrates. For GaN deposited on silicon, the relative intensity of the (0002) XRD peak at 34.6° from the GaN thin films is small in comparison to the (400) peak of the silicon substrate as shown by Fig. 1(d). There are three diffraction peaks present, indicating the GaN films deposited on silicon to be polycrystalline structure.

The optical properties of the epitaxial GaN layers were investigated by low-temperature ($T=14$ K) PL measurements. A mercury lamp with an interference filter which

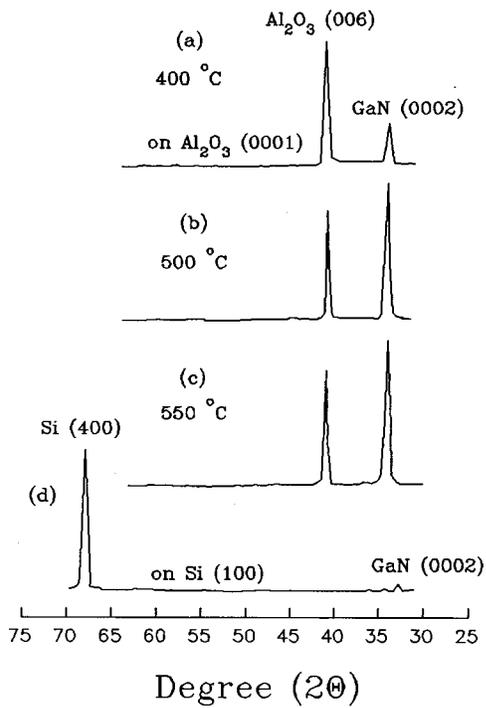


FIG. 1. XRD patterns for GaN films deposited at different temperatures, (a) 400, (b) 500, and (c) 550 °C, on sapphire substrates; also (d) 550 °C on (100) silicon substrates. An AlN buffer layer was deposited at 400 °C prior to the GaN growth. For GaN on Si (100) substrates, all three diffraction peaks for the GaN polycrystalline structure were present. For films deposited on sapphire substrates, only a single diffraction peak from GaN films was observed.

passes only the 257 nm line was used as the excitation source. The photoluminescence spectra were recorded by a high-resolution 1 m monochromator (Acton Research) in conjunction with a cooled photomultiplier tube. Figure 2 shows the spectra of as grown epitaxial layers deposited at four representative temperatures, which shows that the spectral shape depends strongly on the growth temperature. For the epitaxial layers grown at 650 °C, the dominant emission was observed at about 3.47 eV. This emission line is due to the recombination of excitons bound to neutral donors (called I_2 line), which has been observed by many groups previously.⁷⁻¹² The prevailing view is that the donors are due to native N-vacancy defects. However, for epitaxial layers grown at temperatures below 550 °C, the exciton emission line was completely absent and impurity lines were dominating. Furthermore, for layers grown at temperatures above 650 °C, the ratio of the impurity luminescence intensity to the exciton emission intensity is enhanced. Therefore the photoluminescence data show that films grown at 650 °C are of the highest quality. The results shown in Fig. 2 are quite revealing. They indicate that structure characterization such as XRD alone is not sufficient for characterizing the quality of the crystals, as we see that the XRD data in Fig. 1 show similar results for films grown above 500 °C and nonetheless the photoluminescence data show that the exciton emission intensity and hence the crystalline quality depend strongly on the growth temperature.

There are three major luminescence emission lines asso-

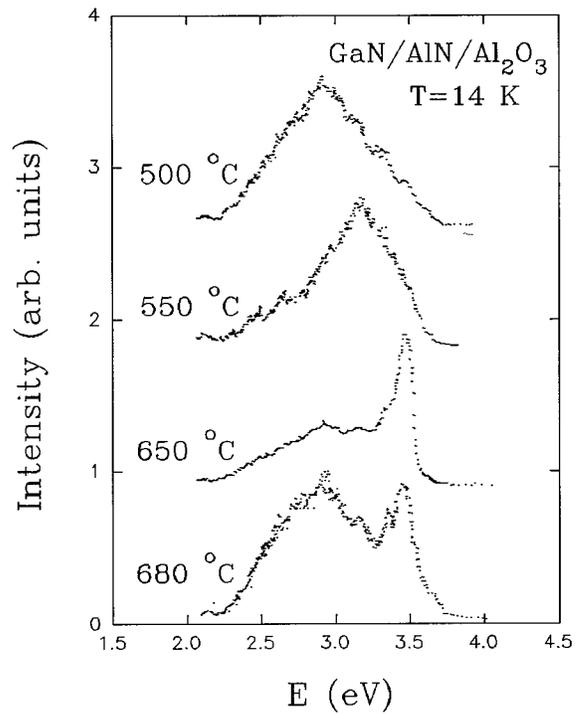


FIG. 2. Low-temperature ($T=14$ K) photoluminescence spectra of GaN films deposited at four different temperatures on sapphire substrates.

ciated with epitaxial GaN films deposited on sapphire substrates, the I_2 line and two impurity related emission bands. For films deposited at 680 °C, all three emission lines can be observed most clearly, the I_2 at 3.47 eV, a line at about 3.2 eV which has been ascribed as being due to the donor-acceptor pair recombination,^{7,8,12} and a line at about 2.9 eV. There is some ambiguity in determining the exact energy positions of the impurity luminescence bands observed here due to the fact that deep level related emission in GaN is broad in nature.⁷ For the films grown at 500 °C, the 2.9 eV emission line dominates. For films grown at 550 °C, the 3.2 eV emission line dominates, but the emission spectrum can actually be fitted by two Gaussian lines with peak positions at 3.2 and 2.9 eV, respectively. The impurity luminescence bands observed here are similar to those observed previously in Mg, B, P, and Zn impurity doped GaN.⁷ Intentional defect incorporation with Mg, B, P, and Zn results in basically two distinctive emission bands near 3.2 and 2.9 eV irrespective of the impurity species. It was pointed out previously that the origin of the deep level formation in GaN is intrinsic in nature.¹³ In our samples, the chemical nature of impurities are unknown. However, analysis with x-ray photoemission spectroscopy indicated that the predominant impurities in the films were oxygen probably originating from an adsorbed surface layer and carbon originating from the pump system. There is some evidence that the residual donors in GaN are caused by the presence of oxygen impurities rather than N-vacancy defects.¹⁴ There is also speculation that carbon can form acceptorlike states with a binding energy of about 860 meV.¹⁵ However, a detailed understanding has not yet been achieved. At this stage, the possibility of a oxygen or carbon related complex being responsible for the impurity

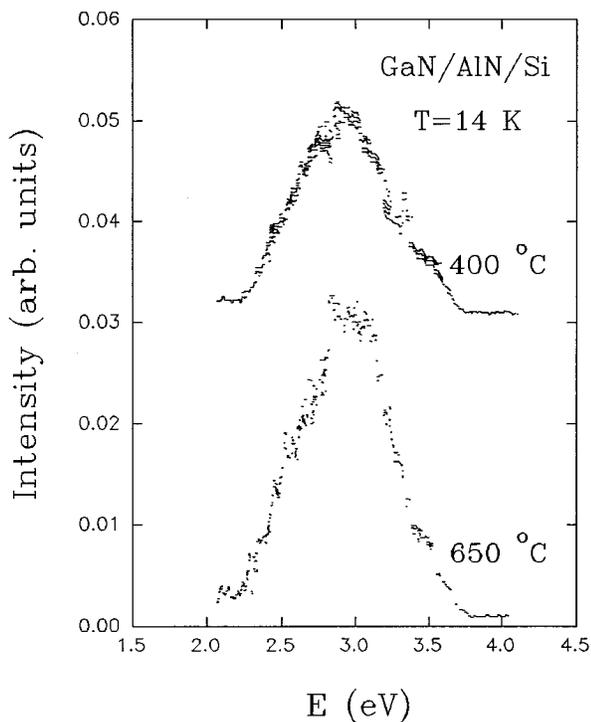


FIG. 3. Low-temperature ($T=14$ K) photoluminescence spectra of GaN films deposited at two different temperatures on silicon substrates.

luminescence observed in the films cannot be precluded. On the other hand, there is also strong evidence that stacking faults are common in all of the GaN films, despite their orientational quality.¹⁶ So a structural defect related complex could be another candidate that is responsible for the impurity luminescence observed here. Nonetheless, the impurity emission bands observed here are approximately in the same energy region as those in impurity doped samples, which again indicates the intrinsic nature of the deep level formation in GaN, which is consistent with the previous interpretation.¹³

The polycrystalline films grown on the Si substrates were also characterized by photoluminescence measurements. Representative results are shown in Fig. 3 for films deposited at temperatures of 650 and 400 °C, both of which show that the exciton emission band was completely absent in the polycrystalline films. The impurity emission spectral shape is almost identical to that observed in the films deposited at 500 °C on the sapphire substrates, and a deep level emission at about 2.9 eV is again dominating. In polycrystal structures, due to the structural disorder, one would expect that the microscopic configuration around the defects is different from that of the defects in single crystals. However, due to the broadness of the defect emission lines, no significant change in the peak position nor in spectral shape was observed in polycrystalline films, which indicates that the origin of the deep center formation in GaN may be irrespective of the crystal quality and relates only to the intrinsic nature of GaN. Previously, common features of the silicon deep donor centers in crystalline and amorphous semiconductor $\text{Al}_x\text{Ga}_{1-x}\text{As}$ have been investigated and the results sug-

gested that there may exist a common description for deep centers in crystalline and amorphous semiconductors.¹⁷ The similar optical spectroscopy results observed in polycrystalline and single-crystal GaN here together with previous work⁷ on impurity doped GaN once again suggest that one may be able to seek a common description for deep level defects in all semiconductors.

In conclusion, epitaxial growth of GaN layers on sapphire substrates have been achieved by MOCVD at a deposition temperature as low as 400 °C by controlling the source gases at a very low flow rate and by first depositing a thin AlN buffer layer at 400 °C. Subsequent photoluminescence characterization indicates films grown at 650 °C are of the highest quality, in which a dominant peak at 3.47 eV attributed to radiative recombination of excitons bound to neutral donors has been observed. This transition was masked by impurity transitions in films grown at temperatures above 650 °C and was completely absent in epitaxial films deposited at temperatures lower than 650 °C. Our results present here seem to suggest that the origin of deep level formation in GaN is irrespective of chemical species as well as of the crystalline quality and is indeed intrinsic in nature. Furthermore, the results shown here indicate that photoluminescence is a powerful technique for characterizing the crystalline quality and structural characterization alone is not sufficient. More importantly, our results show that low-temperature growth of GaN by MOCVD is possible and the quality of the crystal can be optimized by controlling the growth temperature.

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