Growth and Characterisation of Al$_{1-x}$Cr$_x$N Thin Films by RF Plasma Assisted Pulsed Laser Deposition

Brendan J. Arnold, Satheesh Krishnamurthy, Brian Kennedy, Declan Cockburn, Daniel McNally, James G. Lunney, Robbie Gunning, M. Venkatesan, J. Alaria, J. Michael, D. Coey, and Cormac McGuinness

School of Physics, Trinity College Dublin, College Green, Dublin 2, Ireland

J.-H. Guo

Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

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I. INTRODUCTION

Thin films of AlN, CrN and Al$_{1-x}$Cr$_x$N were grown epitaxially on c-axis sapphire by radio frequency (RF) plasma assisted pulsed laser deposition (PLD). The PLD growth mode employed for these Al$_{1-x}$Cr$_x$N films was by delta doping layers of CrN 0.05-0.10 nm thick between layers of AlN of approximately 3.6 nm thick giving an estimated 1.3% and 2.5% Cr doping. The substrate temperature, nitrogen pressure and power parameters of the RF plasma were varied to optimize crystalline growth. X-ray diffraction (XRD) confirmed hexagonal wurtzite thin film growth of highly crystalline AlN and highly crystalline cubic CrN. The electronic structure of these thin films was examined by x-ray absorption (XAS) and soft x-ray emission spectroscopy (XES) at the N $K$ edge. These measurements are compared with the results of density functional calculations for wurtzite-AlN, cubic-CrN and wurtzite-Al$_{1-x}$Cr$_x$N.

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I. INTRODUCTION

The group III-nitride AlN is already firmly ensconced in the semiconductor industry as it has the largest band gap–6.2 eV in the wurtzite phase–among the nitrides making it particularly attractive for optoelectronic devices that need to operate in the blue or violet end of the visible light spectrum. Several applications are in use due its high surface acoustic velocity in addition to its physical and thermal robustness which allows devices using AlN to operate at high temperatures and high powers. Further, tuning of the band gap and the emission wavelength in optoelectronic devices can be realised by doping with Ga forming similarly robust Al$_{1-x}$Ga$_x$N ternary alloys.

Recently, attention has turned to the doping of AlN with ferromagnetic metals which, in common with such doping of GaN, has the potential to realise a dilute magnetic semiconductor. Theoretical work on a number of wurtzite III-V systems has indicated that doping of AlN with ferromagnetic metals such as Mn or Cr should result in room temperature ferromagnetism [1]. In fact, previous experimental work by Yang et al. on Al$_{1-x}$Cr$_x$N films grown by reactive sputtering have shown these films to exhibit ferromagnetism with $x = 0.357$ at higher than room temperature (340K) [2]. They concluded that the ferromagnetic coupling of Cr gave rise to these results. Neither Cr and CrN clusters within AlN are expected to give rise to ferromagnetic behaviour as they are antiferromagnetic materials [3]. However, a more recent study by Ney et al. of RF plasma assisted MBE grown epitaxial CrN films on MgO(001) and sapphire (001) revealed that CrN may under such strained conditions be ferromagnetic. A question arises as to whether strained CrN rather than substituted Cr gives rise to ferromagnetism in Al$_{1-x}$Cr$_x$N thin films. Further, it should be noted that it has already been observed in Ga$_{1-x}$Cr$_x$N doped films grown by MBE that with excess Cr content there is a tendency to form cubic CrN clusters within the film, which is confirmed by the octahedral coordination of Cr inferred from Cr $L_{2,3}$ edge XAS spectra [4].

Another application of Al$_{1-x}$Cr$_x$N films is the area of surface coating technology where such coatings have shown extremely high mechanical hardness as well as corrosion resistance. The mechanical and structural properties of Al$_{1-x}$Cr$_x$N films grown by pulsed laser deposition have been studied extensively by Hirai et al. [5]. They found that with excess doping of Al in Cr$_{1-x}$Al$_x$N above $x = 0.75$ the crystal structure underwent a transition from rocksalt crystal structure to a wurtzite phase. Thus the structural, electronic and magnetic properties of Al$_{1-x}$Cr$_x$N as well as the distribution of dopants in the growth process are all sensitively interlinked and deserve further investigation. How closely interlinked these are has been studied theoretically by Cui et al. in a density functional theory calculation where they have concluded that Cr atoms tend to segregate to form Cr–N–Cr bonded clusters which tend to be either antiferromagnetic or ferromagnetic explaining much of the experimental results to date [6]. For example, the statistical distribution of these embedded clusters is sensitive to growth conditions and in particular temperature; in one instance 1D Cr-rich regions form at 700°C and 0D Cr-rich spherulites form at 800°C [7]. The electronic structure of such inhomogeneously doped systems can potentially be investigated through localised probes of the densities of states such as element specific x-ray spectroscopies like x-ray absorption and resonant soft x-ray emission.

To this end we have chosen to investigate the growth of Cr-doped AlN thin films by the pulsed laser deposition (PLD) method. This has previously been well established for the growth of doped GaN films [8] while the improved
growth of pure AlN films in and RF plasma assisted PLD process has been detailed by Basillais et al. [9, 10].

To elucidate the manner by which a nominally homogeneously doped Al_{1-x}Cr_{2}N behaves, if such a non-clustered doped III-V nitride can exist [6], we have purposely chosen to study a non-homogeneously doped Al_{1-x}Cr_{2}N thin film where we δ-dope by forming closely spaced thin layers of CrN in AlN. The growth of these Al_{1-x}Cr_{2}N films by PLD is described here as well as the physical, optical, electronic, magnetic and x-ray spectroscopic and theoretical investigations into these films.

II. EXPERIMENT

Samples were deposited on c-cut sapphire, Al_{2}O_{3}(001), using radio frequency (RF) plasma assisted pulsed laser deposition (PLD) in a similar experimental setup to that used by Basillais et al. [9–11]. The ablation targets used were separate pure metal Al (99.998%) and pure Cr (99.98%) targets. The sapphire substrates were first annealed in high vacuum (∼10^{-7} mbar) at 850°C for two hours before cooling down to a deposition temperature which was varied between room temperature and 850°C to obtain the best growth. The RF nitrogen plasma source, an Oxford Instruments OSPrey, was kept on both during the deposition and for two hours afterward whilst the sample was cooling to approximately 250°C before the source was de-activated and cooling continued to room temperature in a constant flow of pure N_{2} gas (99.995%). It was intended that this combined post-annealing would allow for stress relaxation in the layers while maintaining stoichiometry in the surface layer. The RF plasma source was typically operated with an RF power of 350W. The chamber pressure during plasma operation and during the deposition was maintained at 1.0×10^{-3} mbar. The pure metal targets were ablated by pulses of laser light of approximately 25 ns duration and wavelength of 248 nm from a KrF excimer laser. Fluences varied between 1.0 and 2.1 J/cm². AlN and CrN growth was investigated first with optimum parameters given in Table I.

Growth of a doped Al_{1-x}Cr_{2}N thin film was performed by alternating laser pulses between the differing pure metal targets where the ablation from a given target was for a defined period of time resulting in a delta doping of the films. The thickness of the alternating layers of AlN and CrN were approximately 3.5 nm thick for the AlN and for the CrN ranged between approximately 0.05-0.1 nm thick. Thus this has given a range of doping concentration of between 1.3%-2.5% for the Al_{1-x}Cr_{2}N thin films.

III. RESULTS AND DISCUSSION

The thin films were primarily physically characterised by x-ray diffraction (XRD) using a Cu Kα Siemens D500 powder diffractometer or a Philips X’Pert Pro for φ-scans, grazing incidence scans and rocking curves. XRD measurements of the PLD grown AlN and CrN films are shown in Fig. 1 and clearly indicate the growth of highly crystalline films of wurtzite AlN and cubic CrN respectively on the sapphire substrate. The observed in plane orientations with respect to the AlN(001) surface are AlN[101] and AlN[110] for CrN/sapphire; thus there is a 30° rotation of the interfacial hexagonal cell between film and substrate in both cases. In the case of AlN, this corresponds to results previously published by Vispute et al. [12].

Figures 2(a) and 2(b) show the XRD peaks of the AlN and CrN thin films respectively with variation in deposition temperature. The insets show rocking curves for a typical film. The w-AlN thin film’s (002) peak shows a variation with deposition temperature with optimum growth near 850°C (Fig. 2(a)). An asymmetric shoulder may be observed which can be attributed to strain at the film, substrate interface which has been reported by Six et al. [13]. Figure 2(b) shows the CrN (111) peak

| Material       | Temp. | Fluence | Repetition rate | Pressure |
|----------------|-------|---------|-----------------|----------|
| Optimal AlN    | 850   | 1.9     | 10              | 1×10^{-3}|
| Optimal CrN    | 700   | 1.3     | 10              | 1×10^{-3}|
| Doped AlN      | 750   | 1.9     | 10              | 1×10^{-3}|
| Doping CrN     | 750   | 1.3     | 1              | 1×10^{-3}|

FIG. 1: 2θ XRD scans of a PLD grown CrN film (top) and a PLD grown AlN film (bottom), both on an Al_{2}O_{3}(001) substrate.
FIG. 2: Variation of the XRD peaks of (a) AlN [002] and (b) CrN [111] with substrate growth temperature. The insets show a rocking curve of these peaks at a particular temperature. Also (a) shows the effect of a lower laser fluence in the growth of an AlN film and the XRD peak of a δ-doped Al$_{1-x}$Cr$_x$N film. Where a gradual reduction in the peak area and intensity is observed with decreasing substrate temperature. Insets show the rocking curves over the peaks AlN (002) and CrN (111) with full-widths of 0.56° and 0.77° respectively.

Figure 2(a) also shows the results of an XRD scan on a ∼1.3% doped Al$_{1-x}$Cr$_x$N thin film. The deposition parameters were as in Table I. The repetition rate of the KrF laser was also reduced from 10 Hz to 1 Hz for the CrN layers to enable finer control of the high yield Cr ablation. The XRD results of these preliminary doped samples show a much lower count from crystal planes than for pure AlN indicating much poorer crystallinity. However, we believe that this can be improved with further refinement of the technique.

The Al$_{1-x}$Cr$_x$N films were magnetically characterised by SQUID measurements in a MPMS XL from Quantum Design but after subtraction of the diamagnetic background arising from the sapphire substrate, no discernible ferromagnetism was observed at room temperature.

**FIG. 3**: Tauc plot of the optical absorbance of an AlN and two doped Al$_{1-x}$Cr$_x$N thin films. Figure 3 shows the Tauc plots of the optical absorption spectra of the AlN and doped Al$_{1-x}$Cr$_x$N films [14]. These were plotted from absorption measurements performed on a Perkin Elmer Lambda 900 dual beam spectrophotometer. The optical band gap for all films is close to 6.0 eV which corresponds closely to the x-ray measurements and is similar to the published band-gap of $\gamma$-AlN of 6.2 eV.

The AlN samples are transparent thin films, the CrN samples are metallic-like thin films, while the Al$_{1-x}$Cr$_x$N thin films are also transparent but with an observable brown tinge. Figures 4(a) and 4(b) show the surfaces of the films under an optical microscope at 200× magnification for depositions at 1.9 and 1.0 J/cm$^2$ respectively. Droplets are clearly visible on both films and are similar to those reported by Basillais et al. [9]. The droplet density is greatly reduced by lowering the fluence, however the crystal quality also reduces at lower fluences–independent of thickness—as is shown in Fig. 2(a) for a film deposited at 850°C at 1.0 J/cm$^2$.

The electronic structure of nitride materials may be studied through various methods including optical characterisation as well as x-ray spectroscopic methods such as x-ray absorption (XAS), and soft x-ray emission spectroscopy (XES). These two x-ray spectroscopic methods probe the unoccupied and occupied densities of states of a material on an element-specific and orbital angular mo-
ment specific basis governed by dipole selection rules. XAS and XES measurements were performed at beamline 7.0.1 at the Advanced Light Source, Berkeley, California. XAS was measured both by total electron yield (TEY) using the drain current method and by total fluorescence yield (TFY) by a channeltron facing the sample positioned 30° above the incoming beam. Measurements at the nitrogen K-edge probe the unoccupied (XAS) and occupied (XES) nitrogen 2p partial density of states (PDOS) of the material. The resolution of the XES spectrometer was 0.4 eV at a photon energy of 400 eV while the monochromator was set to a resolution of 0.4 eV during the XAS scans. The energy scales of the XAS were calibrated by comparison to h-BN while those of the x-ray emission spectrometer were calibrated by Co L$_\alpha$ and L$_\beta$ emission lines in 2nd order.

Figure 5 shows a combination of x-ray spectroscopic results from both pure CrN thin films, pure AlN thin films and two doped Al$_{1-x}$Cr$_x$N films with $x = 0.013$ and $x = 0.025$ respectively. Shown are nitrogen K-edge XAS fluorescence yield (TFY) and drain current measurements (TEY) as well as the nitrogen K-edge soft x-ray emission (XES) spectra of the same samples. The XAS and XES spectra obtained at the nitrogen K-edge are both governed by the dipole selection rule and thus these spectra represent the nitrogen 2p conduction band and valence partial band density of states (PDOS) respectively. The AlN results are also compared to earlier work by Duda et al. [15] while the CrN results are compared to the work of Takeuchi et al. [4].

AlN is a wide bandgap semiconductor and as the conductivity of this sample was very low as it was intentionally undoped the N K-edge XAS spectrum was best measured through fluorescence yield (TFY). The results obtained in this manner from the PLD grown sample are in good agreement with those from an n-type MBE grown AlN film where both XAS spectra are measured in grazing or near-grazing incidence geometry [15]. For the CrN, which is near metallic, the N K-edge XAS whether by TEY or TFY agree very well with each other and with previous studies of MBE grown CrN thin films [4]. Examining the onset of the N K-edge XAS more carefully in Fig. 5, we clearly see that the two doped films have significantly increased spectral weight in comparison to the AlN film at the absorption threshold between 396 and 399 eV which coincides exactly with the measured TFY XAS spectrum from the pure CrN film thus confirming the influence of the CrN layers on the N K-edge TFY XAS.

The TEY of the doped samples, from which a downward trending background has been removed, is also revealing as it shows a peak in each of the doped samples at ~398 eV in coincidence with the peak in the CrN XAS spectrum. Immediately after this peak, the TEY in the doped samples becomes distorted from that observed for the CrN film as it would appear that the dips in the TEY signal at ~400.2 eV are coincident with the peaks in the AlN TFY spectra, where the AlN layers appear to have a much stronger absorption, reducing the yield from the CrN layers. It is speculated that the peak seen in TEY in the AlN sample may arise from a nitrided interface layer between the Al$_2$O$_3$ and AlN as the remainder of the TEY signal differs considerably from that of the doped samples.

The XES spectra from the AlN and the two Al$_{1-x}$Cr$_x$N thin films shown in Fig. 4 were all obtained with the same excitation energy of 400 eV. The AlN XSE spectrum is in very good agreement with that previously obtained from MBE grown AlN samples where these have a greater instrumental broadening [15]. The XES spectrum reflects the nitrogen 2p PDOS of the valence band and should differ from the undoped sample to the doped samples where hybridization of the occupied N 2p states with the Cr 3d states should become more evident. A more detailed comparison of these XES spectra is shown in Fig. 7 where we note the small difference close to the valence band maximum close to 393 eV with increased doping and the significant increased spectral weight with doping between the energies of 390-392 eV which appears to broaden the main N 2p XSE feature and shift the centroid of this peak to lower energy by about 0.3 eV. This contrasts with the behaviour observed in Ga$_{1-x}$Cr$_x$N samples, where the only significant change in spectral weight in the XES spectra or N 2p PDOS was observed just above the valence band maximum with increase in Cr doping [16].

To examine the origin of these spectral differences further some theoretical calculations were carried out. The density functional theory (DFT) calculations presented here employ the full-potential linearized augmented plane-wave (FP-LAPW) method as implemented in the Wien2k code [17]. The recommended standard settings of the code were used as well as the generalized gradient approximation (GGA) of Perdew et al. [18]. The electronic structure for wurtzite w-AlN was computed using the ob-
FIG. 6: Comparison of the N 2p PDOS calculated for AlN, CrN and an Al$_{1-x}$Cr$_x$N $x = 0.125$, as well as the total Al PDOS and Cr PDOS of the Al$_{1-x}$Cr$_x$N.

erved crystal structure (space group $P6_3mc$) and the experimentally determined lattice constants of 3.112 Å and 4.982 Å as inputs [19] while c-CrN has a space group of $Fm\bar{3}m$ and a lattice constant of 4.140 Å. In each case no further geometry optimization was performed. The radius of the muffin tin spheres in w-AlN was 1.78 Å for both Al and N, and in the case of c-CrN was 1.83 Å for N and 2.06 Å for Cr. The total and partial densities of states (DOS) were obtained by $k$-integration over the Brillouin zone. In the case of w-AlN this represented a sampling on a $12 \times 12 \times 6$ mesh leading to 114 irreducible points in the Brillouin zone while for c-CrN the sampling was on a $12 \times 12 \times 6$ mesh leading to 47 irreducible points in the Brillouin zone. The calculated DOS and nitrogen 2p PDOS of AlN was found to be in agreement with that of Jonnard et al. [19] while no such calculations for CrN appeared to be available. A spin polarized calculation of a doped Al$_{1-x}$Cr$_x$N was also performed with one Cr substituted for Al in a 2$\times$2$\times$1 supercell, an equivalent doping of $x = 0.125$. The same lattice parameters as those of wurtzite AlN were used and the Brillouin zone sampled on a mesh of $4 \times 4 \times 4$ leading to 32 irreducible points in the zone.

Figure 6 compares the results of these calculations where the AlN PDOS has been shifted to allow for the overlap of the main occupied 2p PDOS to coincide between the calculations for comparison purposes. The N 2p PDOS for the Al$_{1-x}$Cr$_x$N $2 \times 2 \times 1$ cell is divided into those N sites which are neighbours of the Cr dopant and those N sites which are not neighbours. It can be seen that there is a appreciable N 2p PDOS immediately above $E_F$ only for those nitrogen sites that are beside the Cr and whose 2p states hybridise with the Cr unoccupied 3d levels. Further, for the Al furthest away from the Cr substitution within the 2$\times$2$\times$1 cell there is greater hybridisation between the Al 3p orbitals and the N 2p$_z$ along the hexagonal c axis leading to a more sharply peaked feature, which is evident at higher Cr doping levels in Fig. 5. This can be thought of as being due to the unoccupied and occupied electron density being polarised towards the Cr atom and more involved with bonding to the eg electrons in the valence band and the largely empty spin up and totally empty spin down t$_{2g}$ electrons at or just above the Fermi level. This hybridised unoccupied N 2p density of states is most clearly seen in the TEY XAS spectra.

Figure 7 shows some details of the XAS onset in the TFY where even within the TFY the increased density of states below the conduction band minimum of AlN due to the increasing doping with Cr is clearly seen. Also shown in Fig. 7 are difference spectra of the N K-edge XES of the doped films where with increasing doping it is evident that there is an increasing spectral weight on the lower energy side of the main AlN emission peak. This corresponds to the PDOS shown in Fig. 6 where the occupied PDOS of the N atoms neighbouring the Cr, due to their bonding and hybridisation with occupied Cr 3d levels, gives a broader shoulder to the main feature towards increasing binding energy. Moreover, the sharp non-bonding peak as
is seen in the AlN and in the nitrogen sites furthest away will steadily decrease as the density of Cr atoms increases within an $\mathrm{Al}_{1-x}\mathrm{Cr}_x\mathrm{N}$.

IV. CONCLUSIONS

The physical structure, morphology and electronic structure of pulsed laser deposition grown $\delta$-doped $\mathrm{Al}_{1-x}\mathrm{Cr}_x\mathrm{N}$ films with nominal $x$ values of $\sim 1.3\%$ and $2.5\%$ were studied. While it was apparent that films of wurtzite AlN and cubic CrN could be grown successfully it would seem that a $\delta$-doping or layered doping strategy has neither resulted in ferromagnetic thin films, to be expected if the Cr–N–Cr are either antiferromagnetic or ferromagnetic as evidenced through calculations; nor have thin films of good crystalline quality been obtained as of yet. However, the x-ray spectroscopic results do show clear evidence from the Al $\delta$-doped films produced here of the spectral features that are similar to those that might be expected from a homogeneously doped $\mathrm{Al}_{1-x}\mathrm{Cr}_x\mathrm{N}$ thin film. Detailed measurements from purposeful nanostructuring of the distribution of dopants in proposed dilute magnetic semiconductor materials may prove to be a useful tool in experimentally determining the role, and interplay of the physical and electronic structure with the magnetic behaviour of such systems and warrants further directed investigations in the case of $\mathrm{Al}_{1-x}\mathrm{Cr}_x\mathrm{N}$.

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