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Ferromagnetism and spin polarization in indium nitride, indium oxynitride, and Cr substituted indium oxynitride films

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ABSTRACT

We have investigated the structural, electrical, and magnetic properties of both sputter deposited indium oxynitride and Cr substituted indium oxynitride films as well as InN films grown by molecular beam epitaxy. The degenerate oxynitride films exhibit n-type carrier concentrations in excess of 10^{20} cm^{-3} and remain conducting to low temperatures, while the InN samples have much lower carrier concentrations and are insulating at low temperatures. At the same time all of these films show a room temperature ferromagnetic signal, with saturation magnetization ranging from 0.05 emu cm^{-3} for the indium oxynitride and InN films to 0.30 emu cm^{-3} for the Cr substituted film. Low temperature point contact Andreev reflection measurements find a spin polarizations from $46 \pm 2\%$ for indium oxynitride to $50 \pm 2\%$ for the Cr substituted films. These results highlight the potential of nitrides for spintronic applications.

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There has recently been considerable interest in semiconductors exhibiting room temperature ferromagnetism, in large part because of the possible technological applications of these materials in spintronics [1]. Motivated by theoretical work predicting such properties in a number of transition metal substituted semiconductors [2] and early experimental observations of such behavior in Co-doped TiO_2 [3], and Mn- and Co-doped ZnO [4], among others, there has been a large body of work dedicated to identifying new dilute magnetic semiconductor (DMS) systems. More recently, it has become apparent that weak ferromagnetism can also arise in defect-rich semiconductors in the absence of magnetic dopant ions, as has been observed in TiO_2 [5] and In_2O_3 [6]. However, in a number of cases the weak ferromagnetism has been attributed to magnetic clusters [7], impurity phases [8], or accidental contamination [9]. For many potential spintronics applications, the degree of spin polarization, which is expected to be relatively insensitive to impurity phases, is an important measure of materials performance. This had led to an increasing interest in characterizing potential DMS materials through spin polarization measurements [10,11] in addition to magnetization studies, as in the case of $In_{1-x}Mn_xSb$, for example, which shows re-entrant magnetic behavior [12].

While the majority of the experimental studies on room temperature ferromagnetic semiconductors have focused on oxides, there have been a number of intriguing results on magnetic order in transition metal doped III–V materials, specifically transition metal doped InN. Both Cr and Mn substituted InN films have been studies [13,14]. Molecular beam epitaxy (MBE) grown Mn substituted InN films were found to exhibit a spin glass phase at low temperatures, while Cr substituted samples showed room temperature ferromagnetism [13]. The magnetism in Cr substituted InN was confirmed using X-ray magnetic circular dichroism [14]. Moreover, recent calculations indicate that indium vacancies and nitrogen interstitials in InN are magnetic, the formation of the latter are particularly favorable for n-type material [15]. In vacancies have also been proposed to lead to ferromagnetic order in InN films grown on Al_2O_3, with the structural defects arising from the lattice mis-match [16]. The presence of large concentrations of oxygen in InN can dramatically modify the electrical properties of the material, leading to increases in both the band gap and carrier concentration. Because such oxynitride films remain conducting over a wide range of temperature, they are ideally suited for direct measurements of the low temperature spin polarization. We have

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also studied high quality InN films prepared by molecular beam epitaxy (MBE), having a negligible oxygen content, which allow us to distinguish intrinsic effects in InN from properties arising from possible oxide impurity phases.

The indium oxynitride and Cr substituted oxynitride films used in this study were deposited by rf magnetron sputtering from indium oxide targets in a nitrogen atmosphere. The sputtering targets were prepared using standard solid state reactions from In_2O_3 powder (99.99% pure, Alfa Aesar) with appropriate amounts of chromium chloride ($CrCl_3{\cdot}6H_2O$) added to provide 2 at%, or 5 at% Cr in the composite. These films were deposited on *c*-axis oriented sapphire substrates at $475 \pm 5\,^{\circ}C$ to avoid the dissociation of nitrogen during growth process. Previous studies had shown that certain sapphire substrates showed a small intrinsic magnetization [17]; we used substrates known to exhibit only a small diamagnetic signal, developing a very small ferromagnetic signal on vacuum annealing (as shown in Fig. 3a). The thickness of the films, measured using cross-sectional scanning electron microscopy and confirmed by the interference fringes in optical spectra, was approximately 1 μm. The high quality InN films were prepared using molecular beam epitaxy (MBE) on sapphire substrates with a buffer layer of GaN on AlN, as described in detail elsewhere [18].

Detailed results on the structural properties of the films are discussed elsewhere [19]. The XRD patterns for the oxynitride film can be completely indexed to the wurtzite structure with no evidence for impurity phases. However, Raman spectroscopy shows modes associated with an In_2O_3 secondary phase; no other impurity phases can be discerned. Depth dependent XPS measurements show a highly oxidized surface, with an oxygen content of approximately 25% at depths of over 4 nm [19]. Although these films are isostructural with InN, we prefer to identify them as indium oxynitride, rather than oxygen rich InN, in order to emphasize the important role played by oxygen. This nomenclature is consistent with other reports in the literature having similar oxygen fractions [20].

We show the XRD pattern for the 5 at% Cr substituted indium oxynitride in Fig. 1a; the diffraction pattern for the 2 at% Cr sample is similar. These peaks can be completely indexed to the InN wurtzite structure (JCPDS 50-1239), and are consistent with a polycrystalline sample with no impurity phases. However, similar to the undoped oxynitride films, Raman spectra for the Cr substituted films show evidence for In_2O_3 vibrational modes, with the data for 5 at% Cr sample being plotted in Fig. 1b. These In_2O_3 peaks near $220\,cm^{-1}$ and $300\,cm^{-1}$ confirm that some oxide impurity phase is present in these samples, despite their apparent absence in the XRD patterns. We also see a small peak near $200\,cm^{-1}$, we identify with the Raman-silent B_1 mode in InN, which can be activated by the presence of disorder in the lattice [19]. We do not find any direct evidence for ferromagnetic impurity phases in either the XRD or Raman data. In particular, we do not see any Raman peaks characteristic for ferromagnetic CrO_s [21]. In order to more carefully exclude the possibility of Cr-rich impurity phases, we plot the Cr XPS spectrum for the 5 at% Cr-doped InN film in Fig. 1c. This can be fit assuming that Cr is present only in the 3+ valence state, consistent with substitutional doping.

The oxygen present in the oxynitride films produce an n-type carrier concentration of $3.8 \times 10^{20}\,cm^{-3}$, observed in both Hall effect measurements (not shown) and plasmon absorption, consistent with our previous studies [19]. The optical spectra for the 2 at% Cr substituted oxynitride sample measured with a Perkin-Elmer UV–Vis spectrometer are shown in Fig. 2a, plotted as $(\alpha E)^2$ versus E, with the data for the 5 at% Cr sample being quantitatively similar. These curves are linear at higher energies extrapolating to the optical bandgap energy of approximately 1.8 eV for both samples. This bandgap is consistent with other oxygen-rich InN films [22]. At lower energies, near 0.7 eV, there is a large absorption

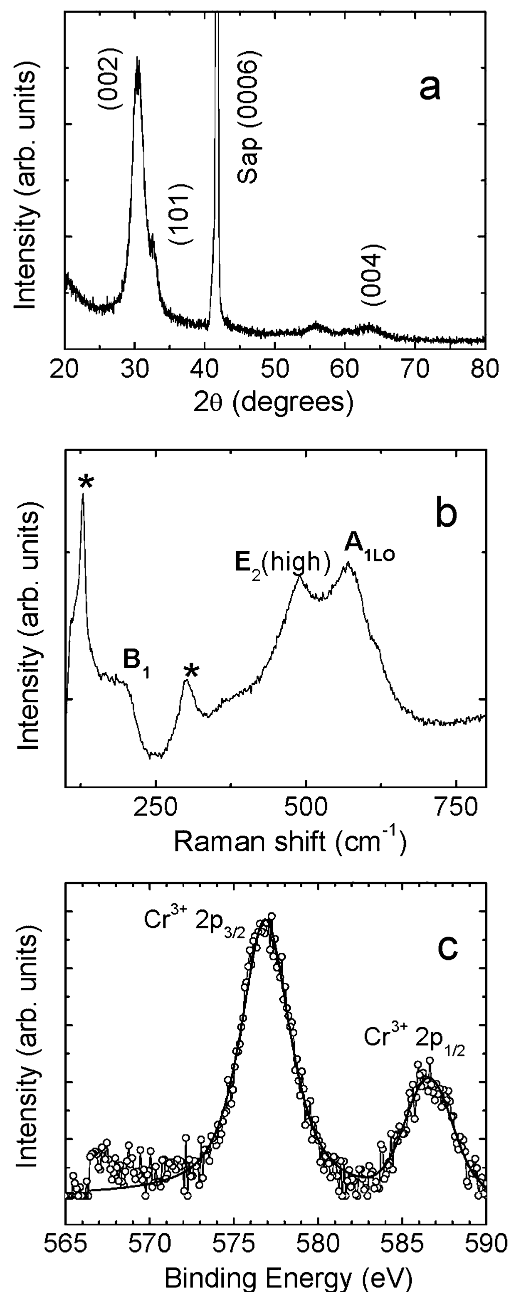

Fig. 1. (a) X-ray diffraction peaks for the 5% Cr substituted indium oxynitride. The sapphire peak is indicated. (b) Room temperature Raman spectra for the 5% Cr substituted indium oxynitride. (c) XPS spectrum for the 5% Cr substituted indium oxynitride. The solid line is a fit indicating the presence of only the 3+ valence state.

peak, which we attribute to plasmon excitations in these highly degenerate films; we estimate the carrier concentrations to be $6.7 \times 10^{20}\,cm^{-3}$ and $7.2 \times 10^{20}\,cm^{-3}$ for the 2 at% and 5 at% Cr substituted films respectively, with similar values obtained from Hall measurements (not shown). The MBE grown InN film has been previously shown [23] to have an n-type carrier concentration of $6 \times 10^{17}\,cm^{-3}$, roughly three orders of magnitude smaller than the degenerate samples, and precluding low temperature spin polarization measurements.

The resistivity of the Cr substituted films, measured using a standard four-probe technique, is plotted as a function of temperature in Fig. 2b. Both films show metallic resistivity on the order of $1\,m\Omega\,cm$ at higher temperatures, with a shallow minimum at lower temperatures. For the 5 at% Cr substituted film this

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