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Properties of rf-sputtered indium–tin-oxynitride thin films

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Indium–tin-oxide (ITO) and indium–tin-oxynitride (ITON) thin films have been fabricated by rf-sputtering in plasma containing Ar or a mixture of Ar and N_2, respectively. The structural, electrical and optical properties of ITON films were examined and compared with those of ITO films. The microstructure of ITON films was found to be dependent on the nitrogen concentration in the plasma. Increasing the amount of nitrogen in the plasma increased the resistivity and reduced the carrier concentration and mobility of the films. The electrical properties of the ITON films improved after annealing. The absorption edge of the ITON films deposited in pure N_2 plasma was shifted towards higher energies and showed reduced infrared reflectance compared to the respective properties of ITO films. The potential of indium–tin-oxynitride films for use as a transparent conductive material for optoelectronic devices is addressed. © *2003 American Institute of Physics.*
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I. INTRODUCTION

The interesting physical properties of oxynitride thin films have been the focus of extensive research due to their potential application in a wide range of electronic and optoelectronic devices. For example, monometallic and bimetallic oxynitrides have been investigated as catalysts,[1] silicon–tin and lithium-phosphorus oxynitrides have been applied in thin-film lithium-ion batteries for microelectronics,[2] and other oxynitrides have been investigated for either their properties (ZrON,[3] CuON,[4] TaON,[5] NbON)[6] or for specific applications like gas sensors (InON),[7] transparent and conductive layers in optoelectronic devices (InON,[8] ZnON,[9] TiON)[10] and optical or hard coatings (TiON,[10] SiON).[11]

Reactive sputtering is the predominant deposition technique employed to fabricate these oxynitride thin films from either an elemental target in O_2-N_2-Ar gas mixtures or an oxide target in N_2-Ar plasma. By changing the amount of gases in plasma, the properties of the resulting thin films can be tailored between the properties of the respective oxide and those of nitride thin films. However, the reproducibility of the properties of the oxynitride films is very dependent on the sputtering processes and condition of the target, and these can become very complex when plasma is formed by simultaneously using two reactive gases, like oxygen and nitrogen.[5,12]

Indium–tin-oxide (ITO) is widely used as a conductive transparent layer on many electronic and optoelectronic devices. It is an *n*-type degenerate semiconductor, with both substitutional oxygen vacancies and tin contributing to its high conductivity. Too many vacancies in the structure of the film will turn it into a nonstoichiometric film and the conductivity will decrease due to an increase in lattice structural disorder. The high conductivity of the films is due to the high carrier concentration rather than to the carriers' mobility. The high optical transmittance of ITO films is a direct consequence of it being a wide band gap (3.5–4.06 eV) semiconductor:[13,14] the fundamental absorption edge lies in the ultraviolet region and shifts towards shorter wavelengths with an increase in carrier concentration due to the Burstein–Moss effect.[15] Attempts have been made to improve the electrical and/or optical properties of ITO, depending on the technological application, by changing its composition to zinc–indium–tin-oxide,[16,17] or by ion implanting H_2^+ or O^+ ions.[18] Apart from an early investigation[19] on the properties of ITO thin films prepared from targets with different In_2O_3/SnO_2 ratios in various dc sputtering plasma gases (including N_2), there have been no reports, to our knowledge, on indium–tin-oxynitride thin films.

In this work, we report on the properties of indium–tin-oxide thin films fabricated by rf sputtering from an indium–tin-oxide target in plasma containing a mixture of N_2 and Ar gases. The properties of thin films deposited in plasma containing pure nitrogen or $Ar-N_2$ mixture, which will be called hereafter indium–tin-oxynitride (ITON) thin films, are compared with the properties of thin films deposited in pure Ar plasma (ITO). The comparison is made on as-prepared ITO

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and ITON films as well as after annealing. The capability and potential of ITON thin films for application to GaAs- and GaN-based optoelectronic devices as conductive as well as optical material are discussed.

II. EXPERIMENTAL DETAILS

The ITO and ITON thin films were deposited by rf sputtering (13.56 MHz, Nordiko NS2500) from an 6 in. diam indium–tin-oxide $(80\% \, In_2O_3 + 20\% \, SnO_2)$ target. The target–substrate distance was 11 cm and the substrates used were Corning 7059 glass and double polished Si or semi-insulating GaAs wafers. The substrates were cleaned in an ultrasonic bath for 15 min that contained organic solvents, then rinsed with de-ionized water and thoroughly blown dry in nitrogen before being placed in the sputtering chamber. Plasma was formed by high purity Ar and N_2 gases, and their flow was controlled by mass flow controllers. All thin films were deposited on unintentionally heated substrates. The sputtering chamber was pumped down to better than 1×10^{-6} mTorr and the target was cleaned in Ar plasma for 10 min prior deposition of the ITO and ITON thin films at rf power higher than that used for deposition of the thin films. In a previous investigation,[20] rf-sputtered ITO thin films had been fabricated in Ar plasma, under various pressure and power plasma conditions and it was found that ITO films with the lowest resistivity were obtained at 5 mTorr Ar pressure and rf power greater than 200 W, followed by annealing at 400 °C for 2 min. All thin films examined in the present investigation were deposited for 75 min at 5 mTorr pressure and 300 W power but the contents of the gases (Ar and N_2) in the plasma were changed.

The surface morphology and the structural properties of ITO and ITON thin films were examined by atomic force microscopy (AFM) (Digital Instruments, Nanoscope IIIA), x-ray diffraction (XRD) using a Cu $K\alpha$ line 1.54 Å at grazing incidence (Siemens D5000) and Auger electron spectroscopy (AES) (Riber 2000 ASC), respectively. An indication of film bonds was obtained from IR absorbance measurements (BioRad FTS-40A). The electrical properties of the films (resistivity, carrier concentration and Hall mobility) were determined by Hall-effect measurements using the four-probe (indium-pressed contacts) van der Pauw technique (BioRad HL5200). The optical properties of the films were examined by recording the transmittance and reflectance in the UV–visible (vis) spectrum (Varian, Cary 50), as well as in the mid-IR (MIR)–IR spectral range (Bruker IS66B).

All measurements were performed on as-prepared films as well as after annealing at 400 °C in flowing nitrogen in a rapid thermal annealing (RTA) system (Jipelec FAV4). Standard contact photolithography was employed for patterning ITO and ITON thin films using AZ5214 photoresist. The same photoresist was used as a mask during wet etching of the films in 10% HF solution. The thickness of the films was determined by measuring the depth etched using an alpha-step 100 Tencor stylus profilometer.

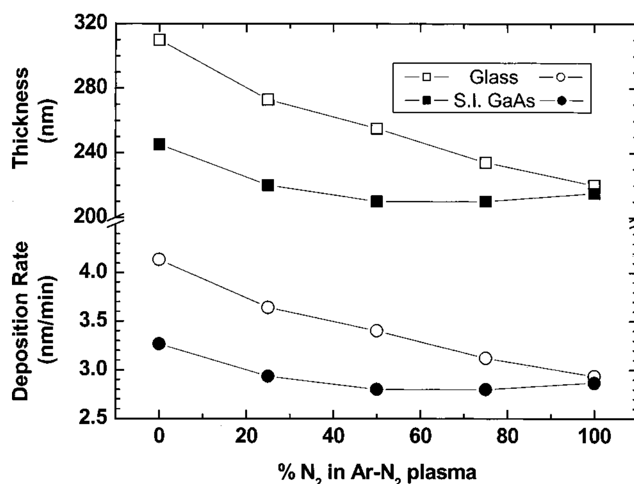

FIG. 1. Thickness and deposition rate of as-prepared indium–tin-oxide films as a function of the percentage of nitrogen in the argon plasma deposited on GaAs and glass substrates (S1-ITO: 100% Ar plasma, S2-ITON: 50% Ar–50% N_2 plasma, S3-ITON: 100% N_2 plasma).

III. RESULTS AND DISCUSSION

A. Deposition rate

ITO films deposited in pure Ar plasma on different substrates, in the same deposition run, resulted in films with different thicknesses, due to the different sticking coefficients of the impinging atoms, as well as to different growth modes of the substrates used. Compared to the thickness of films deposited on GaAs substrates, films deposited on Si substrates were 8–10 nm thinner, whereas films deposited on Corning 7059 glass were 60–70 nm thicker. Introducing nitrogen into the plasma, but keeping the same sputtering conditions, the difference in thickness of the resulting ITON films deposited on different substrates was reduced. Plasma containing only nitrogen gave ITON films with almost the same thickness regardless of the substrate on which they were deposited (within experimental error of ±2%). These results are plotted in Fig. 1, where the thickness of the as-prepared ITO film deposited on GaAs and glass substrates, in the same deposition run, as well as the respective deposition rate, are shown as a function of the amount of nitrogen in the plasma. It can be seen that the biggest change in deposition rate as the amount of nitrogen increases is observed for films deposited on the glass substrate rather than on the GaAs substrate. It is worth mentioning that the thickness of all films was reduced by up to 10 nm after annealing.

A common feature of reactive processes is the hysteresis loop of the experimental parameters upon the introduction of reactive gases into the chamber.[12,21] Due to this phenomenon, a step-like decrease in the sputtering rate is generally seen at a specific partial pressure of reactive gases.[21,22] This nonlinear evolution of the process is caused by poisoning of the target (the formation of a compound on the surface of the target), especially when elemental targets are used and/or two reactive gases (like O_2 and N_2) are introduced into the chamber.[19,21–23] Elimination of this effect is generally achieved by a target conditioning procedure, which is always the first step in such deposition runs.[24] The formation of

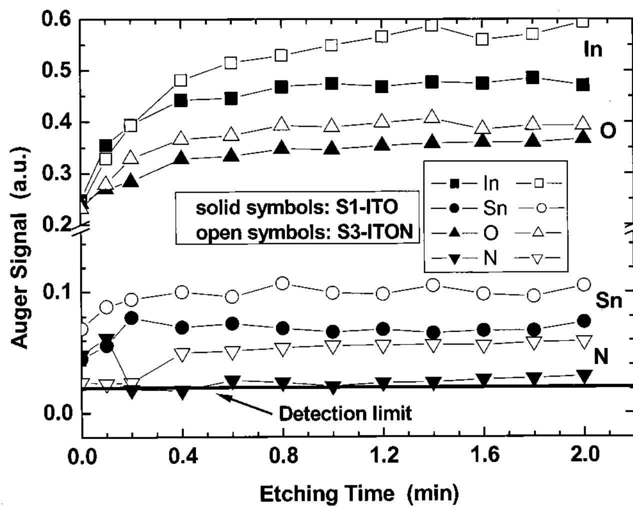

FIG. 2. AES depth profiles of ITO and ITON (100% N_2 plasma) thin films.

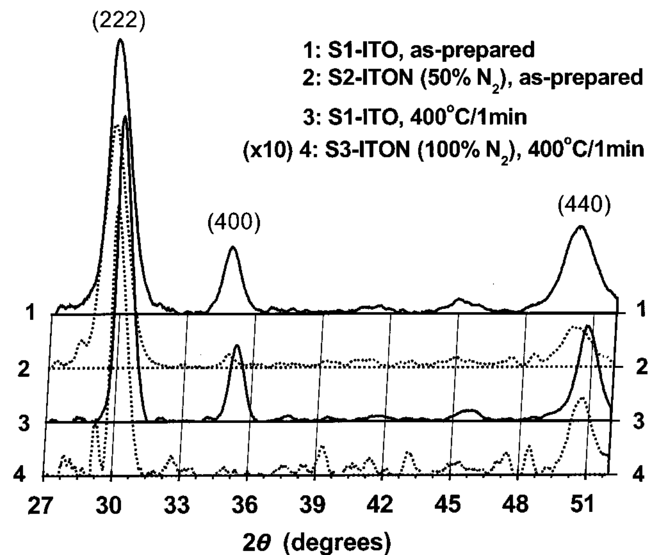

FIG. 3. X-ray diffraction profiles of ITO and ITON thin films just after preparation and after annealing at 400 °C for 1 min.

lower sputtering yield metal–gas compounds at the target, like InN, is not expected on our ITO target because (i) the dissociation energy of indium or tin nitrides is very low (0.2 eV/atom[25]), resulting in a very low sticking probability of nitrogen on the target surface during sputtering due to preferential sputter removal, (ii) we used a metal-oxide target (ITO) instead of a metallic In/Sn target and thus (iii) the use of only one reactive gas (N_2), instead of N_2+O_2 mixture and (iv) there was always a predeposition sputtering run for target conditioning purposes. Thus, the decrease in deposition rate with nitrogen in the plasma, observed in this work, is attributed to the lower nitrogen sputtering yield compared to that of argon.[22,25,26] However, a gradual change of target stoichiometry with the sputtering time due to the different sputtering rates of In, Sn and their oxides[21,27] must not be excluded.

B. Structural properties

1. AES results

The existence of nitrogen in the as-prepared films was examined by AES. Despite the fact that the nitrogen peak (~380 eV) is very close to the In peak (~400 eV) and the observed rapid preferential sputtering of nitrogen during depth profile examination,[8] it was found that nitrogen was not only present in the structure of all films deposited in plasma containing nitrogen but was also homogeneously distributed throughout the structure of the film. This can be seen in Fig. 2, where AES depth profiles of In, O, Sn and N for the S1-ITO and S3-ITON (100% N_2) thin films are plotted. The detection limit of the system is also shown in Fig. 2. The deficiency of the atoms at the surface of both ITO and ITON films is attributed to adsorbed carbon-related contaminants from either the deposition chamber or/and the atmosphere before the AES measurements. It should be noted that In_2O_3 and $In_xO_yN_z$ have been reported to be gas-sensitive materials.[7] Two more features are noticeable in the AES depth profiles of the structures examined. First, there is enhancement of In, Sn and O Auger signals in the presence of nitrogen in the indium–tin-oxide structure (ITON film). This could be related to the degree of crystallinity of the ITO and ITON structures (as will be seen in Sec. III B2. Second, a gradual increase in the signal during etching can be observed for the ITON film, whereas the respective signal for the ITO film is stable. It is anticipated that the presence of nitrogen either in the plasma or/and in the indium–tin-oxide structure has caused the observed increase of the In signal in the ITON film. More experiments are in progress to clarify the above observations and to quantitatively determine the amount of nitrogen in these oxynitride films after deposition as well as after annealing.

2. XRD results

XRD profiles of ITO (S1) and ITON (S2-50% N_2 plasma) thin films just after preparation are shown in Fig. 3 (XRD profiles 1 and 2). The films had a polycrystalline structure with no preferred orientation of the crystallites and, furthermore, the diffraction peaks could not be identified as originating from either cubic In_2O_3, hexagonal InN, SnO_2 or any other known In–Sn–O structures. It has been reported that more than 30% of Sn is needed in order to see clear SnO_2 diffraction peaks.[28] It is worth noticing that the three major In_2O_3 peaks of the (222), (440) and (400) planes at $2\theta=30.58°$, 51.03° and 35.46°, respectively (JCPDS File No. 06-416), are at a 0.5° higher angle at least than those seen in Fig. 3 (XRD profiles 1 and 2). Furthermore, the average lattice spacing, calculated using the Bragg equation,[29] for the strongest peak was 2.969 Å for the ITO film and it increased to 2.978 Å for the film deposited in pure nitrogen plasma (S3-ITON). Such a shift of the diffraction peaks towards lower angles and the subsequent increase of d spacing with an increase in the nitrogen concentration in the plasma have been observed for other oxynitrides[9] as well as for ITO films[30] and they have been attributed to residual stress in these structures.

Annealing the films at 400 °C shifted the diffraction peaks towards higher angles, and the intensities were reduced and new peaks appeared, as can be seen in Fig. 3 (XRD profiles 3 and 4), where the diffraction peaks of the S1-ITO (pure Ar plasma) and S3-ITON (pure N_2 plasma) films are plotted. The three major peaks, after annealing, can now be ascribed to the cubic In_2O_3 structure, with the d spacing of the (222) peak at 30.52° reduced to 2.925 Å for the ITO film and to 2.938 Å for the S3-ITON film. It should be noted, however, that the signal to noise ratio of the spectrum of the S3-ITON film was much lower than in any other spectrum, indicating a finer crystallite size or a disordered structure.[4]

The release of oxygen or/and nitrogen from the structure, which is generally observed after annealing,[31] has helped in the formation of new phases or the separation of already existing phases in the structure. Such phenomena have also been observed during fabrication of indium-oxynitride films from an In target in plasma containing N_2 and O_2.[25] After a careful examination of the diffraction peaks between 28° and 30° it was revealed that the peak at $2\theta = 28.35°$ of the as-prepared S2-ITON film originated from the substrate used. Furthermore, the peak at $2\theta = 29.25°$ of the S3-ITON film can be ascribed to a disturbed tin-oxide peak [arising from the (113) plane at around 29.74°]. This particular peak could not be observed in the as-prepared S2-ITON structure since, if it were there, it would have been entirely overlapped by the strong peak at 29.99°, but it was observed just above the background noise in the S2-ITON diffractogram after annealing (not shown here).

It should be noted that prolonged annealing (at 400 °C for an additional 5 min) the peaks at $2\theta = 29.25°$ and 30.52° of the S3-ITON film were of almost the same intensity, indicating not only the separation of tin-oxide and indium-oxide phases at these low diffraction angles but also a nearly amorphous S3-ITON structure.

Even though there was no clear indication of any InN phase in the structure of the ITON films, all the as-prepared films had an average crystallite size, as calculated using the Scherrer formula[29] for the major diffraction peak, of around 4 nm, which increased to around 10 nm after 1 min of annealing. No correlation could be made between the crystallite size and the amount of nitrogen in the plasma during deposition of the ITON films. It is believed that the polycrystalline structure of the films just after preparation contained stress or was disordered, and had multiple In–O and In-Sn–O phases, which become less disordered after annealing and have mainly the cubic In_2O_3 structure with reduced lattice spacing and bigger crystallite size. Additional annealing of the ITON films deposited in pure nitrogen plasma would result in a more amorphous structure.

3. FTIR results

Infrared absorption measurements were performed using a gold mirror as the reference and the angle of incidence was 30°. Fourier transform infrared (FTIR) spectra were recorded for the ITO film deposited in pure Ar plasma (S1-ITO) and the ITON film deposited in pure N_2 plasma (S3-ITON), both

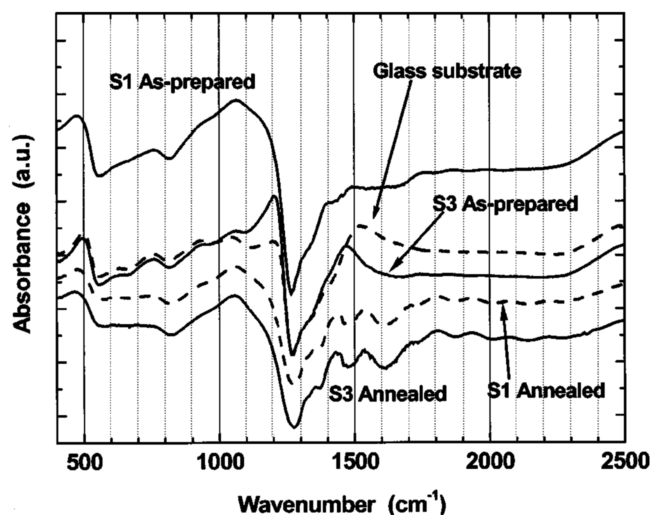

FIG. 4. FTIR absorption spectra of S1-ITO and S3-ITON (100% N_2 plasma) thin films, as prepared and after annealing at 400 °C for 5 min. Also shown is the spectrum of the glass substrate.

deposited on a glass substrate. A spectrum of the glass substrate was also recorded. Figure 4 shows absorption spectra of the S1-ITO and S3-ITON films just after preparation and after annealing at 400 °C for 5 min, as well as the spectrum of the glass substrate.

It can be seen in Fig. 4 that there were specific FTIR features due to the glass substrate. In particular, the features in the region of the spectrum between 900 and 1300 cm^{-1} are associated with asymmetric stretching [longitudinal optical (LO) and transverse optical (TO)] modes of oxygen in Si–O–Si of the glass surface.[32] The peaks, seen in the glass FTIR spectrum at around 1043 and 1198 cm^{-1}, are ascribed to TO and LO modes, respectively. The TO mode is present in the FTIR spectrum of both the as-prepared thin films at around 1063 cm^{-1} and shifts towards 1057 cm^{-1} for both films after annealing, whereas the LO mode is present only in the spectrum of the as-prepared S3-ITON film and it is absent in all the other spectra. From the observed shift in angle of LO and TO modes, it is thought that the glass surface was affected by the deposition of these oxides and there was partial recovery of these effects with annealing. Furthermore, the presence of the LO mode only in the FTIR spectrum of the as-prepared S3-ITON film denotes a strong skin effect in this film,[32] which indicates that the as-prepared S3-ITON film is expected to have higher resistance than the S1-ITON film (as will be seen below). It should be noted that the skin effect is related to the FTIR spectrum features, i.e., the conductivity and plasmon frequency of metal-oxide thin films.[32] No further results related to the above correlations will be presented in this work because it is beyond the scope of this investigation.

At the lower part of the spectra, vibrations from In_2O_3 phase appear at around 606 and 740 cm^{-1}.[33–35] Furthermore, the peak at 1470 cm^{-1}, which appeared only in the FTIR spectrum of the as-prepared S3-ITON film, disappeared after annealing and both films, after annealing, showed two peaks at 1431 and 1536 cm^{-1}. It is believed that the peak of the as-prepared S3-ITON film at 1470 cm^{-1} is associated with the incorporation of nitrogen in the structure and the forma-

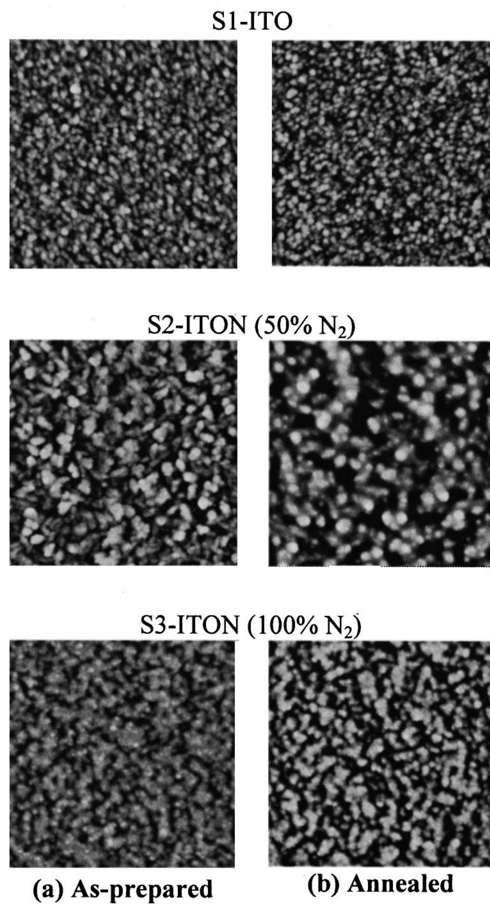

FIG. 5. Surface morphology of ITO and ITON thin films examined by AFM, just after preparation and after annealing at 400 °C for 1 min. Area $=1\ \mu m \times 1\ \mu m$; z scale $=20$ nm.

tion of a nitride-related vibration mode, which disappears after annealing with outdiffusion of nitrogen from the structure. From the two peaks at 1431 and 1536 cm^{-1}, which are present in both films after annealing, the former is ascribed to Sn–O–Sn vibrations, whereas the latter is due to the glass substrate. Sn–O–Sn or Sn–O vibrations must also be responsible for the FTIR features at 1805, 1931, 2080 and 2216 cm^{-1}.[36]

The IR absorption spectra of the ITO and ITON films showed that annealing promotes the formation of new bonds in the structure, which is in agreement with the XRD results in which In–Sn–O phases were observed. Since FTIR results on In–Sn–O thin films are limited in the literature, more experiments are needed for precise identification of the phases and related bonds that exist in ITO and ITON structures.

4. Surface morphology

Examination of the surface morphology of the as-prepared ITO and ITON thin films by AFM revealed that increasing the amount of nitrogen in the plasma resulted in ITON films with an apparent increase in crystallite size. Figure 5(a) shows AFM results of the films just after preparation; the respective surface roughness, deduced from the AFM measurements is given in Table I. It should be remembered that no correlation was deduced from the XRD results presented earlier between the crystallite size and the nitrogen concentration in the plasma. Furthermore, even though the surface roughness of the S3-ITON film was greater than that of S1-ITO film (see Table I), the biggest roughness was observed for the film deposited in the plasma containing mixture of N_2 and Ar, the S2-ITON film.

The annealing process modified the surface appearance of the ITON films but not that of the ITO film. Figure 5(b) shows AFM images of the film after annealing at 400 °C for 1 min. It can be seen that there is an apparent increase in grain size for the ITON film after annealing, which is in accordance with the observations from XRD measurements.

It is believed that the introduction of nitrogen into the plasma resulted in ITON films with disturbed grains and defects in the structure. This disturbed structure resulted in the observed shift in angular position of the XRD diffraction peaks but not in the increase in grain size, which is contradictory to the apparent increase in crystallite size observed by AFM. These phenomena are more profound when both Ar and N_2 are present in the plasma during deposition of the films and have generally been observed for rf-sputtered nitride thin films.[22] The structural changes that took place after annealing eliminated most of the defects and resulted in the diffraction peaks being at angles expected for a cubic In_2O_3 structure. However, films deposited in plasma with a mixture of N_2 and Ar gases have structures with less packing density than the film deposited in pure nitrogen plasma. Increased porosity has been observed for indium-oxynitride films fabricated in plasma containing 20% N_2–80% Ar.[7]

C. Electrical properties

All ITO and ITON films prepared in this work were n-type degenerate materials as deduced from Hall-effect measurements. Hall-effect measurement results (carrier concentration, mobility and resistivity) were also recorded after annealing the films at 400 °C for 1 min and then for 5 minutes and the results are shown in Fig. 6. The electrical properties of the as-prepared film deposited in pure Ar plasma (ITO) deteriorated with the introduction of nitrogen

TABLE I. Root mean square roughness of ITO and ITON films deduced from AFM. The RTA was 400 °C for 1 min.

	S1-ITO (0% N_2 plasma)		S2-ITON (50% N_2 plasma)		S3-pure ITON (100% N_2 plasma)	
	As prepared	RTA	As prepared	RTA	As prepared	RTA
Roughness (nm)	2.54	2.40	5.27	3.51	3.47	3.05

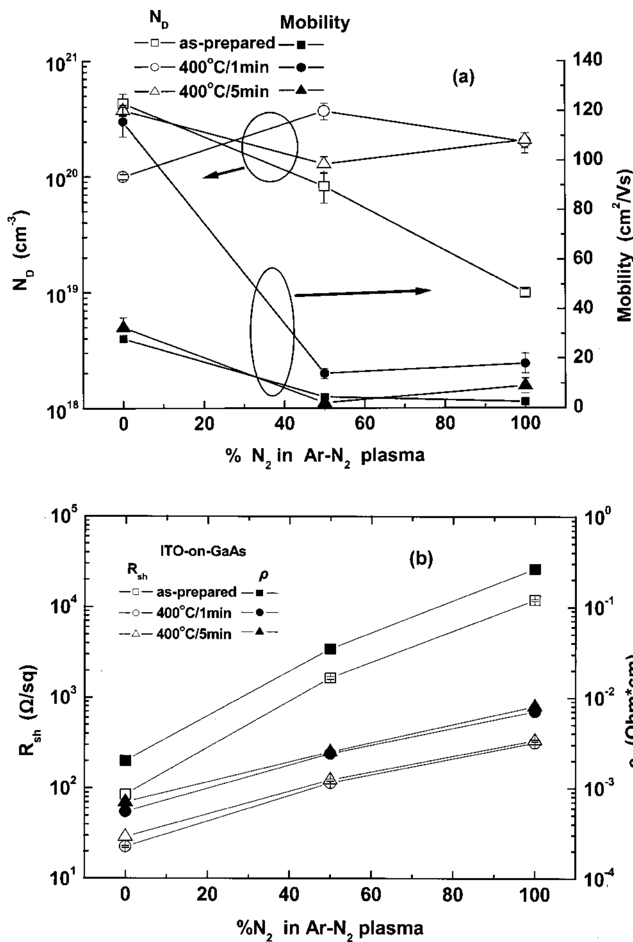

FIG. 6. Hall-effect measurement results just after preparation and after annealing of ITO and ITON thin films as a function of the nitrogen in the plasma. (a) Carrier concentration, N_D, and mobility; (b) sheet resistivity, R_{sh}, and resistivity, ρ.

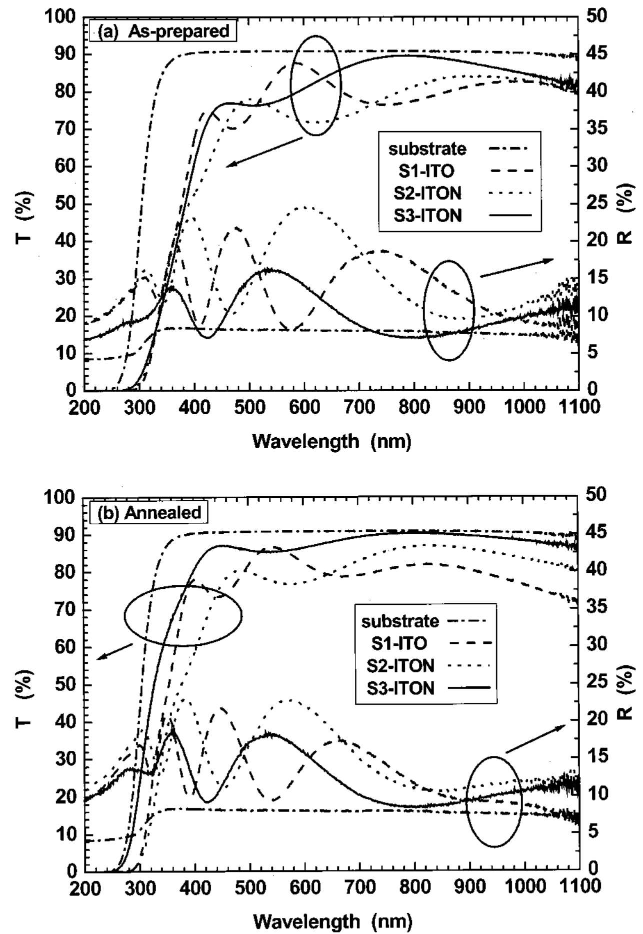

FIG. 7. UV–vis transmittance and reflectance of ITO and ITON films (α) just after deposition and (b) after annealing at 400 °C for 1 min. S1-ITO: 100% Ar plasma; S2-ITON: 50% Ar–50% N_2 plasma; S3-ITON: 100% N_2 plasma.

into the chamber. By increasing the amount of nitrogen in the plasma, the carrier concentration and mobility were reduced and the resistivity increased. ITON films deposited in pure N_2 plasma exhibited electrical properties which were one-to-two orders of magnitude worse than the properties of ITO films. Nitrogen incorporation into indium-oxynitride films has been reported to increase resistivity.[7] The electrical properties of the films improved after annealing, as can be seen in Fig. 6. However, the mobility and resistivity of the ITON films were inferior to those of the ITO film, whereas the carrier concentrations of the two films were almost the same, at least for the annealing conditions used in this investigation.

As shown in Sec. III B, where the structural properties of the films were investigated, the introduction of nitrogen into the structure of the ITO film created defects, which resulted in the reduction of carrier mobility. It is worth noticing, that mobility was reduced almost 80% by changing the plasma content from 100% Ar to 50% Ar–50% N_2, and it was further reduced by around 40% in 100% N_2 plasma. The reduced carrier concentration of the ITON films and, consequently, high resistivity of the films, must be attributed to the occupation of oxygen vacancies by nitrogen. Annealing, where some outdiffusion of oxygen or nitrogen might have taken place, increased the oxygen vacancies and subsequently the carrier concentration of the films. The mobility and conductivity of the ITON films also improved with annealing, but despite the apparent increase in grain size of the annealed ITON films, shown earlier, their structures are more amorphous than polycrystalline, inhibiting further improvement of the carrier mobility and resistivity. It should be noted that the second annealing step (400 °C for 5 min) reduced the carriers' mobility from the improved value they exhibited after the first annealing step (400 °C for 1 min). Noticeable is the remarkably high mobility, around 120 $cm^2/V\,s$, exhibited by the ITO film after the first annealing step.

D. Optical properties

The transmittance, reflectance and absorbance of the ITO and ITON films deposited on the glass substrate, just after deposition and after annealing at 400 °C for 1 min, were examined in the UV–vis spectra (200–1100 nm) at an angle of incidence 10°. These results are shown in Figs. 7 and 8, along with the respective behavior of the uncoated glass substrate. Figure 7(a) shows the transmittance and reflectance of

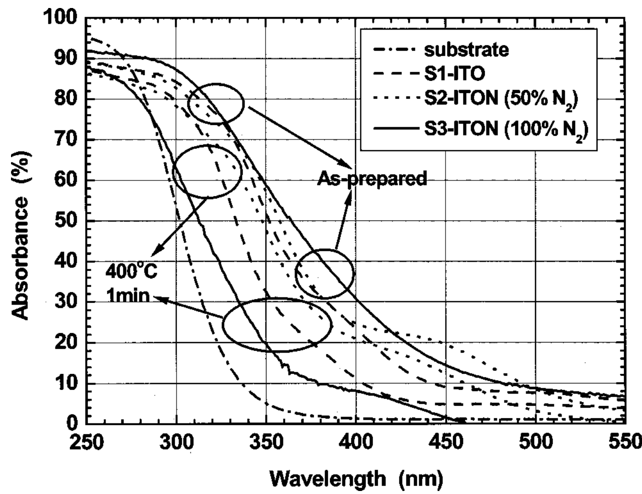

FIG. 8. UV–vis absorbance of ITO and ITON films deduced from the transmittance and reflectance results in Fig. 7.

the as-prepared ITO and ITON films, whereas the absorbance of the films, in the range of 250–550 nm, can be seen in Fig. 8. By increasing the amount of nitrogen in the plasma during deposition the thin film showed an increase in overall transmittance which was more profound for the pure ITON films (S3 film, 100% N_2 plasma). Transmittance is inversely dependent upon free carrier absorption and thus upon the conductivity.[24] The ITON film exhibited higher transmittance than the ITO film, in accordance with the lower conductivity of the film shown earlier. Furthermore, the absorption edges of the as-prepared ITO and ITON films were almost similar.

Annealing of the samples improved their behavior, as can be seen in Figs. 7(b) and 8. The reflectance and absorbance were reduced and the transmittance increased, especially for the pure ITON film (sample S3) in the UV region of the spectrum. However, one important change after annealing was that the absorbance became more abrupt and, furthermore, particularly for the pure ITON film, there was a shift of the onset of transmittance and absorbance towards shorter wavelengths. The shoulder seen at the onset of the absorbance curve of the S2 film (Fig. 8) is associated with increased roughness of the film[37] compared to S1 (ITO) and S3 (pure ITON) films and it is consistent with the increase in reflectance of this film and the AFM observations of its surface (cf. Fig. 5). A similar shoulder seen for S3 film after annealing cannot be exclusively attributed to surface roughness, since, as seen by the AFM photos of Fig. 5, the S3 film exhibited less rough surface than the S2 film. It is thought that this kind of roughness must be associated with the appearance of porosity in the film.[7]

By calculating the absorption coefficient, α, of the films, by $T \sim (1-R)^2 \exp(-\alpha d)$, where T is the transmittance, R is the reflectance and d is the thickness of the films,[38] and plotting α^2 as a function of the photon energy (not shown here), the optical energy gap of the films was obtained. Table II shows the calculated optical energy gap values of the ITO and ITON films prepared in this work. As seen in the optical spectra, the absorption edge and therefore the optical band gap of the as-deposited films are comparable. It can be seen, however, that after annealing the optical band gap increased. In both cases, as deposited and after annealing, the optical band gap of the pure S3-ITON films is higher than that of the ITO film. The effect of annealing the indium–tin-oxide films fabricated in pure nitrogen plasma on the energy gap is more pronounced than the effect of annealing the films fabricated in pure argon plasma on the energy gap. The reduced value of the optical energy gap of the S2-ITON film prepared in Ar–N_2 plasma is believed to be associated with defects in the structure, which create states in the band gap. It should be remembered that S2-ITON film has shown structural behavior quite different from that of the S3-ITON film, which was deposited in pure nitrogen plasma.

The change in absorption edge after annealing can be explained by the Burstein–Moss shift.[38] With an increase in free carrier density higher states in the conduction band are occupied which leads in turn to an increase in the optical energy gap. As was shown in electrical characterization of the films, the carrier concentration increased after annealing, so the change in energy gap is attributed to this effect. The much larger energy gap of the S3-ITON film, which in both cases, as deposited and after annealing, has a lower electron concentration than respective ITO films, cannot be explained by the Burstein–Moss shift. It is anticipated that a basic structural change in the band structure of the material with the introduction of nitrogen into the film must have been taken place.

An estimate of the refractive index of the films was also obtained from the optical spectra in Fig. 7. The index of refraction of the ITO film was 2.10, and it increased to 2.18 after annealing, whereas the index of refraction of pure ITON film (S3-pure nitrogen plasma) was 1.64 and increased to 1.81 after annealing. It is known that the refractive index is related to the packing density of the films.[39] The reduced index of refraction of the S3-ITON film, compared to that of the S1-ITO film, is in accordance with the reduced packing density of the film revealed by the AFM images in Fig. 5. Improvement of the index of refraction with annealing is an indication of an increase in the packing density of the structure,[30] which may be associated with the relaxed struc-

TABLE II. Optical energy gap, E_{gap}, of ITO and ITON films deduced from the optical spectra in Fig. 8. The RTA was 400 °C, for 1 min.

	S1-ITO (0% N_2 plasma)		S2-ITON (50% N_2 plasma)		S3-pure ITON (100% N_2 plasma)	
	As prepared	RTA	As prepared	RTA	As prepared	RTA
E_{gap}	3.43 eV 361 nm	3.61 eV 343 nm	3.35 eV 370 nm	3.43 eV 361 nm	3.51 eV 353 nm	3.95 eV 314 nm

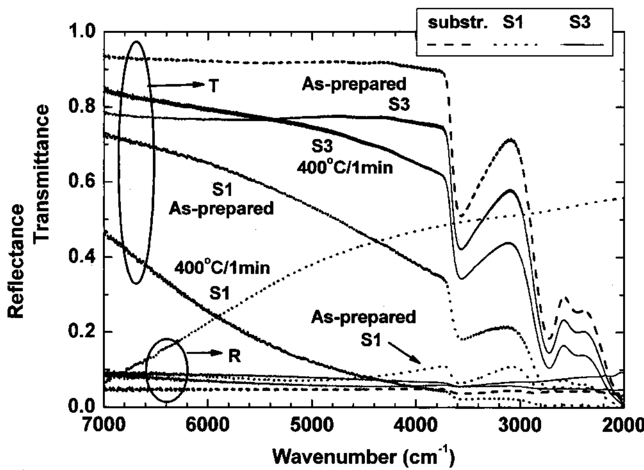

FIG. 9. Midinfrared transmittance and reflectance of ITO and ITON films just after deposition and after annealing at 400 °C for 1 min. S1-ITO: 100% Ar plasma; S3-ITON: 100% N_2 plasma.

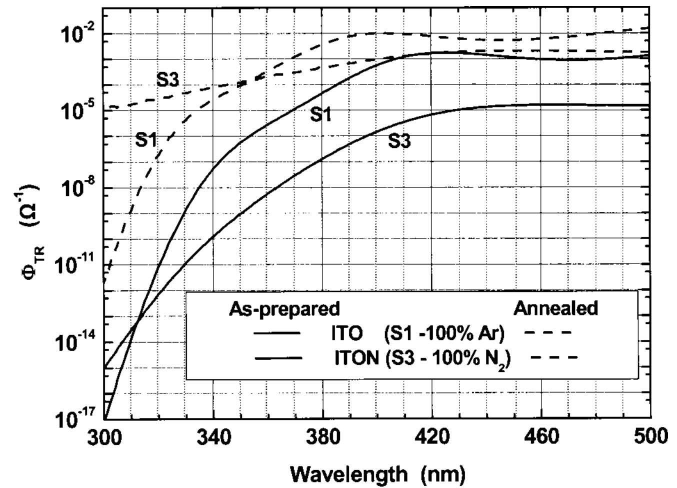

FIG. 10. Figures of merit as a function of the wavelength for ITO and pure ITON films.

ture of these films after annealing, discussed in Secs. III B 2 and III B 3.

The effect of the free carriers on the optical properties of the ITO and pure ITON films in the mid-IR spectrum was examined and the results are shown in Fig. 9. The Drude absorption caused by free carriers is more pronounced in the case of ITO compared to ITON films. Also, after annealing the free carrier absorption is shifted towards higher photon energies, indicating an increase in carrier concentration, which is in agreement with the electrical characterization.

Thus, we conclude that during deposition nitrogen is incorporated into the film by occupying oxygen vacancies. This leads to a change in the band structure as well as to a decrease in the electrical conductivity of the film. After annealing the electrical conductivity increases due to the release of nitrogen, leaving a deficient structure behind.

Apparently there is a substantial increase in the optical energy gap of the annealed pure ITON film compared to in the ITO film after annealing. This makes ITON promising as an optical material for GaN-based optoelectronic devices. It should further be noted that the transmittance of ITON after annealing in the near-IR (NIR) and mid-IR regions is much higher than the transmittance of ITO. Since ITO has also been considered for applications in the telecommunications area (1.55 μm),[30] the present investigation strongly indicates that ITON films are suitable for application in the whole deep UV (DUV)–IR spectral range.

E. Figure of merit

A well-behaved transparent conductive thin film should exhibit transmittance and high conductivity. However, the transmittance and conductivity properties of indium–tin-oxide films are known to have an inverse dependence upon each other. The figure of merit for the optimum value of transmittance and conductivity to obtain the best performance of a thin film is defined by[40] $\Phi_{TR}=T^{10}/R_{\mathrm{sh}}$, where T is the transmittance and R_{sh} is the sheet resistivity of the thin film. The higher the figure of merit, the better the performance of the transparent conducting thin film.

Figures of merit of the ITO and ITON (pure nitrogen plasma) are plotted in Fig. 10 in the wavelength spectrum between 300 and 500 nm. The transmittance values of the films were corrected by taking into account the transmittance of the glass substrate. It can be seen that the figure of merit values of the as-deposited films, particularly of the ITON film, are low. Even though these values improved after annealing, the figure of merit values of pure ITON film were still inferior to the respective value of the ITO film. This is basically due to the high resistivity of the ITON film, despite the fact that its transmittance is higher than that of the ITO film. However, the behavior of the ITON film in the UV-DUV region ($\lambda<350$ nm) is better than that of the ITO film due to the higher energy gap of the ITON film. The use of ITON thin films as transparent conductive layers on devices operating at these wavelengths certainly requires further improvement of the figure of merit value. As mentioned above, this improvement can be realized by reducing the resistivity of ITON films more, which necessitates further investigations be made for the optimal deposition parameters of the layer. In the present work the gas mixture in the plasma was the only variable parameter in the deposition and more experiments are in progress where the total pressure, power and annealing conditions will be the deposition parameters examined in order to produce ITON film with improved conductivity without reducing the transmittance presented in this work.

IV. CONCLUSIONS

Indium–tin-oxide and indium–tin-oxynitride thin films were fabricated by rf sputtering from an ITO target in plasma containing a mixture of Ar and N_2 gases. By increasing the amount of nitrogen in the plasma the deposition rate was reduced, as well as the carrier concentration, mobility and conductivity of the deposited thin films. The electrical properties of the films improved after annealing but the properties of the ITON films were inferior to those of the ITO films, at least for the sputtering deposition parameters and the annealing conditions used in this work. The microstructure of the

ITON films was found to be very dependent on the nitrogen concentration in the plasma. The optical properties (transmittance and reflectance) in the whole DUV–IR spectral range of ITON films deposited in 100% nitrogen plasma improved after annealing compared to the respective properties of the ITO films. In addition, pure ITON films exhibited an absorption edge at shorter wavelengths that was not related to the increase in carrier concentration after annealing. If the enhanced optical properties of these ITON thin films were accompanied by improved conductivity, which can be achieved by preparing ITON films under optimal deposition conditions, indium–tin-oxynitride films would be ideal optical materials for application as transparent and conducting films for optoelectronic devices.

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