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Nitrogen incorporation during metal organic chemical vapor deposition of ZnO films using a remote Ar/N_2 plasma

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Nitrogen-containing zinc oxide films were deposited by the metal organic chemical vapor deposition technique from oxygen/diethylzinc mixtures injected in an argon/nitrogen expanding thermal plasma. Infrared spectroscopy and mass spectrometry measurements suggest that nitrogen is incorporated mostly as –C≡N and segregated at grain boundaries. The correlation between the presence of nitrile bonds and the formation of HCN in the plasma phase points towards an inherent limitation during such deposition process, i.e., when using carbon-rich precursors in a highly reactive nitrogen environment, such as an Ar/N_2 expanding thermal plasma. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2221391]

Zinc oxide (ZnO) is an extensively studied transparent conductive oxide as a valid alternative to indium tin oxide for different applications, ranging from flat panel displays and solar cells to thin film transistors and optoelectronics. With this focus, *n*-type ZnO films with a resistivity as low as 10^{-4} Ω cm and an optical transparency above 80% have been obtained by different deposition techniques, using group III dopants.[1–3] For fabricating ZnO-based optoelectronic devices, however, both *n*- and *p*-type materials are required. Synthesizing *p*-type ZnO is a big challenge because of the presence of native donor defects and low dopant solubility.[4] After the initial studies on *p*-type ZnO films reported by Minegishi *et al.* in 1997,[5] many attempts for achieving *p*-type conductivity using different dopants have been reported.[6–9] Theoretical calculations have shown that nitrogen is a good candidate for *p*-type doping of ZnO.[10] While nitrogen can incorporate either in atomic or molecular form, literature studies indicated that the atomic one is preferred for achieving *p*-type conductivity.[11] However, the high energy of the N≡N bond (~9 eV) makes dissociation difficult to achieve in most growth techniques. The expanding thermal plasma (ETP) technique used in this work[12,13] might, therefore, be an excellent source for obtaining *p*-type ZnO films due to its reported capability of generating high fluxes of N atoms.[14] Moreover, the ETP technique has already been used to grow high quality natively textured *n*-type ZnO for thin film solar cell applications.[15]

In this letter we report on N-containing ZnO films deposited by expanding thermal plasma metal organic chemical vapor deposition (ETP-MOCVD) technique. We show that N incorporates in the ZnO matrix mainly as nitrile bond (–C≡N), as evidenced by infrared absorption spectroscopy in combination with elastic recoil detection (ERD) analysis. Moreover, a clear relation between the –C≡N presence and ZnO electrical and structural properties is reported. This important finding has implications for all processes in which a combination of a metal organic (carbon-rich) Zn precursor and activated nitrogen is used to grow *p*-type ZnO. In these cases, N doping efficiency is significantly limited because of the CN formation, which takes place most probably already in the gas phase, as evidenced by mass spectrometry investigations.

We used a cascaded arc plasma source (p_{arc} =300–600 mbars, I_{arc}=50 A) operated on argon [Φ_{Ar} =840–2000 SCCM (SCCM denotes cubic centimeter per minute at STP)] to generate a plasma, which expands into a low pressure deposition chamber ($p_{reactor}$=1 mbar). A high density of N radicals [above 10^{12} cm^{-3} (Ref. 14)] is produced by admixing N_2 with Ar in the cascaded arc channel (Φ_{N_2}=0–150 SCCM). Diethylzinc [$Zn(C_2H_5)_2$, DEZ; Φ_{DEZ} =5.15 SCCM] and oxygen (Φ_{O_2}=20–150 SCCM) are admixed downstream in the expanding plasma, where they are dissociated in interactions with reactive species produced in the arc, i.e., N radicals, argon and nitrogen ions. Since the electron temperature in the downstream region is low (<0.3 eV), electron induced dissociation products can be neglected.[16]

Under O_2-poor conditions, i.e., Φ_{O_2}<60 SCCM, the carbon content of the films was found to increase from less than 0.2 at. % to higher than 0.8 at. % and to correlate with the nitrogen incorporation, which increased from 0% to 0.5%, as determined from ERD measurements. This was confirmed by infrared spectroscopy, which showed the presence of an absorption line at 2203 cm^{-1}, associated with the nitrile bond (–C≡N) stretching vibration.[17,18] As shown in Fig. 1, its concentration increases with nitrogen flow. Important to notice is that the CN peak full width at half maximum is very small (<10 cm^{-1}), when compared to usual bulk nitrile peaks in carbon nitride films (>100 cm^{-1}).[19] This might

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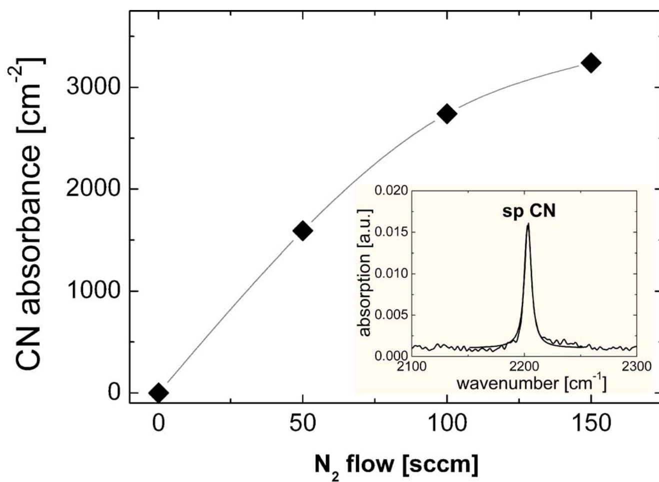

FIG. 1. (Color online) The C≡N integrated absorbance (normalized to the film thickness) as a function of the nitrogen flow for films deposited under O_2-poor conditions ($\Phi_{O_2}=50$ SCCM). Inset: the IR region where the C ≡N absorption (2203 cm^{-1}) occurs together with the Lorentzian fit used for determining the peak area.

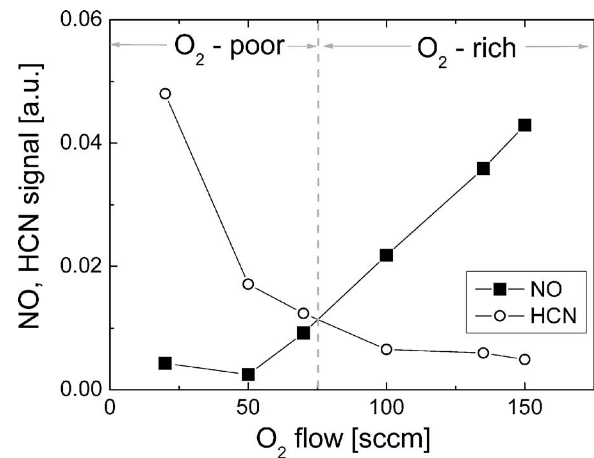

FIG. 2. Mass spectrometry results on the HCN and NO formation in the background of an Ar/DEZ/O_2/N_2 plasma ($\Phi_{N_2}=50$ SCCM). The measured signal is normalized to the He signal (constant flow) in order to correct for pressure changes in the mass spectrometer/plasma reactor.

suggest that CN bonds are mainly present at the grain boundaries in N-containing ZnO. By taking into account the literature-reported values for the infrared absorption cross section of the nitrile bond in carbon nitride films[20] and the N content in the films resulted from ERD measurements, we can estimate that at least 30% of the nitrogen incorporates as –C≡N. The presence of other N–X bonds (X =H,N,Zn,O) is not observed in the infrared absorption region. N_2 is not infrared active and N–Zn stretching vibration lies outside the investigated frequency range. N–H bonds are also not observed and their importance can be excluded since a cross section comparable to the one of C≡N is found in literature [i.e., for the stretching vibration at 3350 cm^{-1}, the cross section is in the range of 10^{-24} m^2 (Ref. 21 and 22)]. As far as N–O bonds are concerned it can only be concluded that their absorption is below the detection limit of the Fourier transform infrared (FTIR) spectrometer.

It is noteworthy that a clear proof for the nitrile bond presence was obtained, despite the fact that the N density in our films is lower than the typical values reported in literature. Both Keyes *et al.*[23] and Barnes *et al.*[24] detected other chemical environments than CN as being dominant. Previously, only Nickel *et al.*[25] suggested the –C≡N bond presence in the ZnO films on the basis of infrared spectroscopy. In their case, the feature appears shifted towards 2240 cm^{-1}, pointing out to a different local environment of the CN bond, and is broad, suggesting CN incorporation within the grains.

Mass spectrometry measurements show that nitrogen is incorporated when HCN is formed in the plasma, i.e., under O_2-poor conditions (see Fig. 2). This suggests that –C≡N formation and incorporation in the films originate directly from gas phase reactions of nitrogen species with hydrocarbon fragments formed during the dissociation of DEZ. Remarkably, whereas NO is one of the proposed precursors for p-type doping,[26] no nitrogen incorporation is observed when abundant NO is formed in the gas phase, i.e., under O_2-rich conditions ($\Phi_{O_2}>100$ SCCM) (see Fig. 2), as determined by means of ERD measurements.

To clarify the effects of CN incorporation, we studied the electronic and microstructural properties of the (C)N-containing ZnO films obtained by ETP-MOCVD. No significant change in crystallinity or optical transmission was found upon nitrogen addition. The x-ray diffraction (XRD) and transmission measurements showed (002) preferential orientation and high transmittance in the visible range (85%), respectively, for all films.[27] The electrical properties, on the other hand, changed. The four point probe measurements indicated an increase in resistivity with the incorporated CN (see Fig. 3). From Hall measurements, performed at room temperature, we determined n type conductivity for all films and a decrease in mobility decreased with CN incorporation, causing the increase in resistivity (see inset of Fig. 3).

Since no deterioration of the film crystallinity upon nitrogen addition was observed, i.e., no decrease of grain size along the (002) direction [(002) peak width], the mobility decrease can be attributed to an increased electron-impurity scattering.[28] This conclusion, together with the relatively constant carrier concentration (see Fig. 3), indicates that CN is electrically inactive, acting as an impurity scattering center. This is evidenced by the linear dependence of the inversed mobility with the CN absorbance. We, therefore, conclude that –C≡N behaves differently in the ZnO films reported here than the $(C{=}N)^{2+}$, recently investigated by means of density functional theory calculations by Limpi-

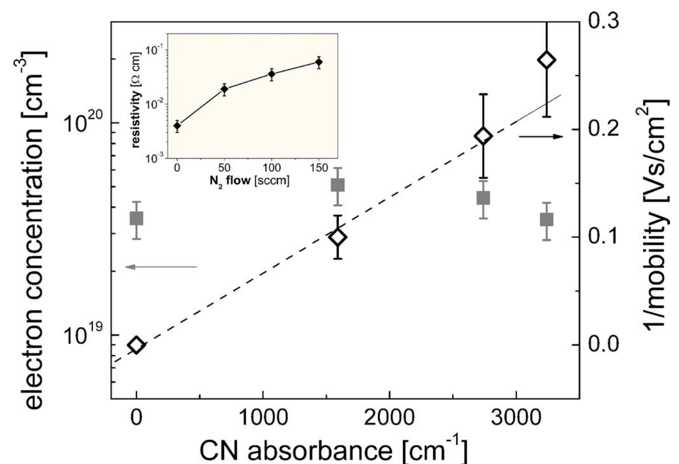

FIG. 3. (Color online) The electron density and inversed mobility as determined from Hall measurements as functions of the CN absorbance. Inset: the resistivity of the N-doped ZnO films changes upon nitrogen addition.

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jumnong *et al.*[29] In that case, CN is predicted to act as a donor when incorporated at an O site. To conclude, we incorporated N in ZnO films obtained using the expanding thermal plasma technique, under O_2-poor conditions. A nitrogen content of about 0.5 at. % was determined (ERD), mainly in the form of nitrile bonds. CN is found to be electrically inactive, behaving as an impurity and possibly segregated at grain boundaries, as suggested by the FTIR and XRD measurements. Our results imply that undesired CN incorporation will occur in any ZnO:N deposition process using a metal organic Zn precursor and nitrogen-containing gas in a highly reactive nitrogen environment.

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