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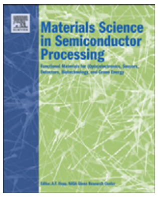

Carrier gas and VI/II ratio effects on carbon clusters incorporation into ZnO films grown by MOCVD

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ABSTRACT

Undoped ZnO films were deposited by atmospheric metal-organic chemical vapor deposition (MOCVD) on (0001) ZnO substrate. The films were grown at various partial pressure ratios of oxygen and zinc precursors (VI/II) using either N_2 or H_2 as carrier gas. Micro-Raman scattering was employed to study the effects of carrier gas, VI/II ratio and annealing on carbon impurity incorporation into the ZnO films. Besides the well known phonon modes of ZnO, Raman spectra of the samples grown with N_2 carrier gas show two additional broad peaks, which are ascribed to carbon sp^2 clusters related modes, spreading in the frequency range 1300–1600 cm^{-1} and dominate the Raman spectrum of the sample grown under oxygen deficiency (VI/II=0.25). In addition, a band centered at $\sim 520\ \text{cm}^{-1}$, considered as some defects related local vibrations, appears in the samples grown with N_2 as carrier gas and its intensity increases when the VI/II ratio decreases. The average cluster size, estimated from the intensity ratio of D over G bands of the carbon sp^2 clusters, ranges from 16.5 to 19.4 Å. However, in all the samples grown with H_2 as carrier gas, the bands related to carbon sp^2 clusters and defects, are largely suppressed and the second-order-Raman scattering band (1050–1200 cm^{-1}) is clearly observed in addition to the bulk ZnO lattice modes. After annealing the samples at 900 °C in oxygen ambient, the crystal quality has been improved for all the samples but the carbon related bands, formed in the as-deposited films grown with the N_2 carrier gas, were only weakened.

1. Introduction

Recently, the behavior of unintentional doped carbon, incorporated into ZnO films fabricated by the MOCVD technique, has obtained more attentions [1–3]. The incorporation of carbon, which is an inevitable impurity, is due to the introduction of metal-organic precursors during MOCVD growth and to the low formation energy of carbon related complexes [4]. Several works have reported the formation of carbon related complexes and carbon sp^2 clusters in doped and undoped ZnO films grown by MOCVD [5–8]. However, carbon related mechanism is not yet clear, which may be a big obstacle for the realization of high quality, as well as p-type conductivity of ZnO films [9,10]. Carbon clusters are indicated by the emergence of the called as D- and G-bands in Raman spectra [5,11]. The G peak is related to the vibrations present in the sp^2 phase, both in the olefinic and ring structures, while the D peak is related to the vibrations of the sixfold rings [12].

Desorption rate from growing surface of residual hydrocarbon radicals, which have been considered as the dominant carbon impurity source, are determined by

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growth conditions [4]. It was reported that high temperature and oxygen atom significantly suppress carbon incorporation rate [6]. Liu et al. found that high growth temperature, VI/II ratio in the gas phase and ionization of oxygen precursor like O_2 and N_2O or addition of H_2 to N_2O can reduce the D and G bands intensity [6,13]. They showed that heterogeneous reactions between Zn species and O species play an important role during the growing process and influence the incorporation rate of carbon impurities, particularly at low growth temperatures. Therefore, the experimental and theoretical analyses performed on ZnO films grown by MOCVD provide understandings of the formation mechanism of carbon related defects.

Actually, p-type conduction of ZnO is not always obtained even after doping with nitrogen as acceptor species [9,10]. Hence, the establishment of defect control is a prerequisite for realizing high quality ZnO, as well as high doping efficiency of nitrogen at a low growth temperature. Reports on the role and behavior of unintentionally doped carbon in ZnO films grown by MOCVD under various growth conditions are scarce. In this work, we have carried out a detailed Raman study on undoped ZnO films grown by MOCVD under various VI/II ratios and using either N_2 or H_2 as carrier gas in order to investigate the influence of growth conditions on carbon incorporation into the ZnO films. The carbon incorporation rate shows a strong dependence on the VI/II ratio for the films grown with the N_2 carrier gas and is largely influenced by the kind of the used carrier gas. In addition, the films were annealed at 900 °C in oxygen ambient to study the annealing effect on carbon incorporation into the samples. Raman measurements show that the use of H_2 as carrier gas suppresses significantly the incorporation of carbon into the ZnO films.

2. Experimental details

ZnO thin films were grown on (0001) O-polar surface of ZnO substrate in an MOCVD reactor. Dimethyl zinc and tert-butanol are used, respectively, as zinc and oxygen precursors. The films were grown at various partial pressure ratios of oxygen and zinc precursors (VI/II) using either N_2 or H_2 as carrier gas. The total pressure is 1 atm for all the depositions, the carrier gas flow rate is 1 l/min and the total flow rate is 2 l/min. The ZnO films were grown at 420 °C with a deposition time of 60 min. The samples growth conditions are given in Table 1. To improve the structural and optical properties, the as-grown films were annealed in oxygen ambient for an annealing time (t_{ann}) of 1 h. The annealing temperature was kept at 900 °C and the oxygen ambient pressure was 1 atm. Raman spectroscopy was used to study the behavior of unintentionally doped carbon in the as-grown and annealed ZnO films. The Raman spectra were performed at room temperature in backscattering configuration using the 514.5 nm Ar^+ laser line for excitation and the incident laser power was 20 mW.

3. Results and discussions

3.1. ZnO films grown with N_2 as carrier gas

Fig. 1 shows Raman spectra of ZnO films which are conducting, transparent and grown at various VI/II ratios using N_2 as carrier gas. The peaks at 436 and 332 cm^{-1} are assigned to the vibrational modes of E_2 (high) (E_2^H) and $2E_2$ (M), respectively [14]. In the high-frequency region, two broad bands called as D (disorder) and G (graphitic), which are ascribed to the local vibration modes of carbon sp^2 clusters, are clearly observed [11,15,16]. In disordered carbon, these modes are related to graphite modes exhibiting A_{1g} and E_{2g} symmetries that are broadened by disorder [17,18]. The D and G bands dominate the Raman spectra when the VI/II ratio decreases. For ZnO film prepared in deficient oxygen condition the amount of carbon incorporated into the sample is much larger (Fig. 1(c)). This results in the pronounced increase of the D and G modes. The presence of carbon clusters is accompanied by a breakdown of the translational crystal symmetry that causes the well known ZnO phonon modes to disappear from Raman spectrum of sample S_{3N}(VI/II=0.25). In the MOCVD growth, the presence of carbon in ZnO is not surprising because of the use of metal-organic precursors. Raman spectra of samples S_{2N} and S_{3N} show also a new relatively intense band centered at ~520 cm^{-1}, which intensity decreases by increasing the VI/II ratio. A similar band with a maximum at 520 cm^{-1} was also observed in undoped and nitrogen doped ZnO films grown by MOCVD [8,19–21]. Some researchers attributed this band to disorder-activated phonon modes particularly interstitial zinc [22]. As seen in Fig.1, when the VI/II ratio increases the E_2^H mode becomes more intense, the bands related to defects and carbon sp^2 clusters modes are largely reduced in intensity and the second order band appears. Also, the peak attributed to the longitudinal optical A_1 mode appears in sample S_{1N} at 577 cm^{-1} but with a weak intensity. These indicate that

Table 1
MOCVD growth conditions of the ZnO samples grown at various VI/II ratios ($P_{t\text{-but.}}/P_{DMZn}$) with N_2 or H_2 as carrier gas.

Sample	VI/II	Carrier gas	DMZn flow (sccm)	t-but. flow (sccm)	P_{DMZn} (Pa)	$P_{t\text{-but.}}$ (Pa)	Thickness (μm)
S_{1N}	1	N_2	30	10	27.8	32.2	2.08
S_{1H}	1	H_2	30	10	27.8	32.2	2.8
S_{2N}	0.5	N_2	30	5	27.8	16.1	3.2
S_{2H}	0.5	H_2	30	5	27.8	16.1	3.7
S_{3N}	0.25	N_2	60	5	55.6	16.1	2.02