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Study of the optical properties and structure of ZnSe/ZnO thin films grown by MOCVD with varying thicknesses

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ABSTRACT

ZnSe layers were grown on ZnO substrates by the metal organic chemical vapor deposition technique. A new structure appeared at lower thicknesses films. The structural properties of the thin films were studied by the X-ray diffraction (XRD) and Raman spectroscopy methods. First, Raman selection rules are explicitly put forward from a theoretical viewpoint. Second, experimentally-retrieved-intensities of the Raman signal as a function of polarization angle of incident light are fitted to the obtained theoretical dependencies in order to confirm the crystallographic planes of zinc blend ZnSe thin film, and correlate with DRX measurements. Raman spectroscopy has been used to characterize the interfacial disorder that affects energy transport phenomena at ZnSe/ZnO interfaces and the Photoluminescence (PL) near the band edge of ZnSe thin films.

1. Introduction

ZnSe is a material belonging to the family of semiconductors. It is optically active in the visible region and has some potential use in thin film devices. ZnSe is a promising material in optoelectronic devices such as light emitters (blue laser diodes), photodetectors and photovoltaic devices, due to its wide band direct gap (2.67 eV) and large bonding energy exciton (21 meV) at room temperature [1]. Charge separation has been facilitated by type-II band alignment of hetero-structures. These structures are composed of two particular semiconductors ZnO and ZnSe [2]. The band gap also makes ZnSe an efficient inorganic sensitizing shell for ZnO to construct heterostructures, aiming at improving the optical properties and broadening the optical region of the ZnO crystal.

In order to achieve a good quality of ZnSe films, many growth techniques have been employed such as metal organic chemical vapor deposition (MOCVD) [3,4], molecular beam epitaxy [5] and photochemical deposition [6]. The MOCVD method is advantageous in growing a high-quality of ZnSe films. A key factor in guaranteeing a higher performance of semiconductor devices is their high crystalline qualities, As regards ZnSe on ZnO, the lattice mismatch between the two materials results in hampering the achievement of a high growth quality at the interface. This affects both the optical and electrical properties of the ZnSe/ZnO heterostructures.

In this paper, thin ZnSe films with different thicknesses were prepared on a ZnO substrate by MOCVD and their structural and optical properties were then analyzed by X-ray diffraction (XRD), Raman spectroscopy and low temperature dependent photoluminescence (PL) spectroscopy. The angle variations of the Raman intensities of allowed phonon modes in crystals with a zinc blend structure were calculated and compared with experimental data extracted from angle-dependent Raman spectra of the ZnSe/ZnO (0001) orientation. The different structural and optical parameters of these films were determined as a function of the thickness. Accordingly, both optical and structural properties on thick sample witnessed a gradual improvement. We notice also the appearance of an additional phase close to the interface.

2. Experimental details

The ZnSe thin films were prepared by metal organic chemical vapor deposition (MOCVD) technique using a vertical reactor operating at atmospheric pressure. The ZnSe thin film is deposited on ZnO substrate at 380 °C. DEZn and ditertiarybutylselenide (DTBSe) are to be used as zinc and selenium precursors in the same

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chamber. The morphology of the ZnSe thin films was studied with scanning electron microscopy (SEM). The crystal structure was analyzed by X-ray diffraction (XRD) using Cu Kα radiation (0.154178 nm). PL measurements were carried out on a Triax 550 spectrometer equipped with a liquid-nitrogen-cooled charged device camera. The samples were immersed in a helium bath cryostat at 4 K.

A Jobin-Yvon T64000 micro-Raman spectrometer was used to characterize the ZnSe thin films. The Raman spectra were performed at room temperature in backscattering configuration using the 488 excitation line of an Ar^+ laser. The laser excitation power was 2 mW. Throughout the Raman experiments, a confocal configuration of the probe was adopted, corresponding to a x50 objective lens and numerical objective aperture 0.42. In order to follow the Raman selection rule discussed above, a half-wave plate was used in order to rotate the incident linear polarization of the laser beam. θ is the angle between the polarization direction of the incident light and growth axis.

3. Results and discussions

3.1. XRD analysis

The structure of the ZnSe thin films was verified with the X-ray diffraction (XRD) method. Fig. 1 shows the XRD patterns of three ZnSe thin films of varying thickness from 90 to 1600 nm. All the films showed the preferred (111) orientation. Other planes (31.07° and 33.05°) appear only at a thickness lower than 0.17 µm, corresponding to the presence of structure other than ZnO wurtzite and ZnSe zinc blend. These 2θ value peaks do not exist in datasheets (fiches ASTM) of ZnSe or ZnO. Also, their relative intensity decreases with increasing the thin film thickness. In contrary, the peak intensity at $2\theta=27.30°$ increases with the increase of the film thickness. Accordingly, increasing the quality of the films for a preferentially orientation along [111] direction exhibits a zinc blend structure with lattice parameter $a=5.63$ Å. The structural parameters of these films was determined using Scherrer formula (1) [7], where λ is the wavelength of X-ray used and β is the full-width at half maximum (FWHM) of (111) peak. The strain (å) and the dislocation density (δ) defined as the length of dislocation lines per unit volume of the crystal were calculated from formula (2) [8].

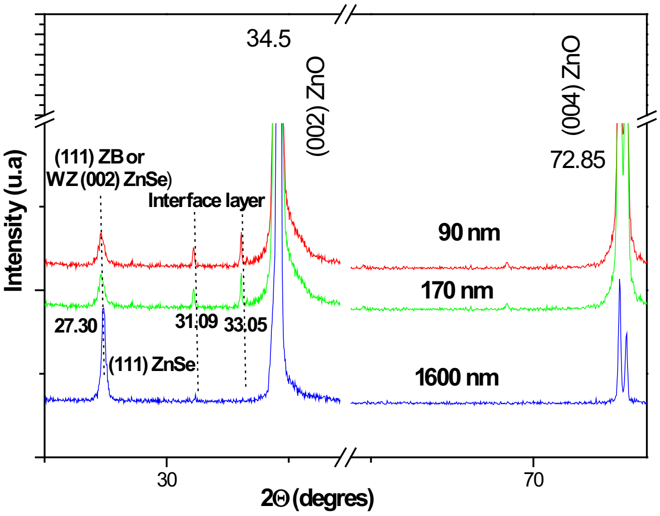

Fig. 1. XRD patterns of three ZnSe thin films having different thicknesses from 90 to 1600 nm.

Table 1
The structural parameters of ZnSe thin films having different thicknesses from 90 to 1600 nm.

Samples	Thickness (nm)	Lattice parameter (Å)	Dislocation density $\delta*10^{14}$ (/m²)	Strain ε $=10^{-3}$ (/m⁴)
S1	1600	5.63	3.46	0.67
S2	170	5.66	8.11	1.06
S3	90	5.69	*13.6*	1.18

$$\delta=\left(\frac{\beta\cos\theta}{0.94\lambda}\right)^2 \tag{1}$$

$$\epsilon=\frac{\beta\cos\theta}{4} \tag{2}$$

Table 1 summarizes the structural parameters deduced from this analysis. It can be observed that these parameters decrease with the increase of film thickness. This reflects the global increase of the structural quality of the material with thickness.

3.2. Raman analysis

3.2.1. Raman selection rules for zinc blend ZnSe structure

In order to get ample information on the crystallographic orientation of the thin film ZnSe, the polarization Raman analysis was used, where the intensity of the Raman scattering $I_R$depends on the Raman tensor R and the crystal symmetry [9]:

$$I_R=\left|\vec{e}_i R(\alpha_{ij})\vec{e}_s\right|^2 \tag{3}$$

where the $\vec{e}_i$ and $\vec{e}_s$ are the polarization of the incident and scattered radiations, respectively. The optical phonon at the Brillouin zone center in the zinc blende structure is splitting into a doubly-degenerate-transverse optical (TO) mode and a longitudinal optical (LO) mode, and the Raman tensor elements are different for the TO and LO modes [10]. When an optical phonon is polarized along the direction $\vec{e}_1=[100]//x$, $\vec{e}_2=[010]//y$ and $\vec{e}_3=[001]//z$, its Raman tensors R_{e1}, R_{e2}, and R_{e3} can be represented by a (3 × 3) matrix. Concerning Raman selection rules, the LO mode is allowed from the (100) plan in the $x(-)x$ configuration, while the TO mode is not allowed in this configuration.

$$R^{xyz}{}_{(x)}\begin{pmatrix}0&0&0\\0&0&1\\0&1&0\end{pmatrix} R^{xyz}{}_{(y)}\begin{pmatrix}0&0&1\\0&0&0\\1&0&0\end{pmatrix} R^{xyz}{}_{(z)}\begin{pmatrix}0&1&0\\1&0&0\\0&0&0\end{pmatrix}$$

In the crystallographic orientation case (111), the selection rule can be determined by the reference change. The Raman tensors are transformed into the laboratory coordinate system with the basis ([111], [0-11], [11-2]). The transformation can be described by the matrices T [11,12].

$$T\begin{pmatrix}\frac{1}{\sqrt{3}}&\frac{1}{\sqrt{3}}&\frac{1}{\sqrt{3}}\\\frac{1}{\sqrt{6}}&\frac{1}{\sqrt{6}}&\frac{-2}{\sqrt{6}}\\\frac{1}{\sqrt{2}}&\frac{-1}{\sqrt{2}}&0\end{pmatrix}\qquad T^{-1}\begin{pmatrix}\frac{1}{\sqrt{3}}&\frac{1}{\sqrt{6}}&\frac{1}{\sqrt{2}}\\\frac{1}{\sqrt{3}}&\frac{1}{\sqrt{6}}&\frac{-1}{\sqrt{6}}\\\frac{1}{\sqrt{3}}&\frac{-2}{\sqrt{6}}&0\end{pmatrix}$$

The Raman tensors $R_{ei}{}^{XYZ}$ in the basis ($X_{111}=[111]$, $Y_{0\text{-}11}=[0\text{-}11]$, $Z_{11\text{-}2}=[11\text{-}2]$) can be described by [12]

$$R_{ei}{}^{XYZ}=TR_{ei}T^{-1}(1) \tag{4}$$

In the backscattering configuration, the wave vectors radiation $\vec{k}_i$ and $\vec{k}_s$, respectively, are both parallel to the [111] axis. To comply with the photon-phonon wave-vector conservation rule, the wave