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Epitaxial ZnO Films Grown at Low Temperature for Novel Electronic Application

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Monocrystalline films of zinc oxide were grown at 300 °C by atomic layer deposition. ZnO layers were grown on various substrates like ZnO bulk crystal, GaN, SiC and Al_2O_3. Electrical properties of the films depend on structural quality. Structural quality, surface morphology and optical properties of ZnO films were characterized using X-ray diffraction, scanning electron microscopy, and photoluminescence, respectively. High resolution X-ray diffraction spectra show that the rocking curve FWHM of the symmetrical 00.2 reflection equals to 0.058° and 0.009° for ZnO deposited on a gallium nitride template and a zinc oxide substrate, respectively. In low temperature photoluminescence sharp excitonic lines in the band-edge region with a FWHM equal to 4 meV, 5 meV and 6 meV, for zinc oxide deposited on gallium nitride, zinc oxide and sapphire substrate, respectively.

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1. Introduction

Atomic layer deposition (ALD) introduced by Suntola in 1980 [1] was originally used to obtain monocrystalline films on monocrystalline substrates. At present ALD is widely used to deposit both polycrystalline and monocrystalline layers, including semiconductors and amorphous high-k oxide films [2, 3]. One of the main advantages of this method is the possibility of low temperature growth. This is also possible on surfaces with highly developed morphology. Characteristic features of the ALD are self limitation and a sequential growth process. This enables the use of very reactive precursors and reduction of a growth temperature, while keeping good crystallographic and optical parameters.

ZnO, which is a II–VI semiconductor with a 3.37 eV direct band gap at room temperature, may be applied in many devices. This includes light emitters, piezoelectric transducers or sensors. ZnO is also a very prospective material for three-dimensional memories [4] and transparent electronics [5], including the ones with an organic material used as an active part of the device [6–8]. For the latter applications low temperature of ZnO deposition is essential [3, 6] and 300 °C is an applier limit here. The ZnO material grown within the above temperature limit is typically polycrystalline. For other applications monocrystallinity of ZnO films is important. Growth methods that are able to produce such ZnO films are pulsed laser deposition (PLD), chemical vapor deposition (CVD) with its modifications (like MOCVD) and molecular beam epitaxy (MBE), but temperatures used for monocrystalline ZnO growth are commonly much higher than 300 °C. They often exceed 600 °C (for reviews see [10] and references therein). However, already it was often claimed that the ALD method is not suitable for the monocrystalline growth. In a previous paper [6] we reported on a epitaxial ZnO growth by the ALD, for films grown on a GaN template. This observation motivated the presented study. We demonstrate that crystalline ZnO can be grown on different substrates like ZnO, GaN, SiC and sapphire at restrictive temperature limit. We analyze structural characteristics of these films and relate layer quality with electrical parameters.

2. Experimental

ZnO films studied here were obtained at 300 °C by the ALD method on GaN, SiC, Al_2O_3 and ZnO templates in the Savannah-100 reactor from Cambridge Nanotech.

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We used diethylzinc (DEZn, $(C_2H_5)_2Zn$) as a zinc precursor and deionized water as an oxygen precursor. The zinc oxide film at the surface was created as a product of the double-exchange chemical reaction of DEZn with deionized water

$$C_2H_5 - Zn - C_2H_5 + H_2O \rightarrow ZnO + 2C_2H_6\,.$$

The structure and the crystallographic orientation of ZnO layers were determined by X-ray diffraction (XRD). The quality of the layers was investigated by a high resolution X'Pert MRD diffractometer equipped with a X-ray mirror and a two-bounce monochromator at the incident beam. The diffracted beam was measured with a 2-dimensional solid-state X-ray detector — PIXcel. The surface morphology and films cross-section images were obtained by scanning electron microscope (SEM, Hitachi SU-70) with an operation voltage of 15 kV. Room temperature photoluminescence (RT PL) studies were performed with a xenon lamp and the CM 2203 spectrometer. Low temperature (LT) PL measurements were obtained with He–Cd 325 nm laser line using the CCD camera.

3. Results and discussion

One micrometer thick films were deposited on substrates with different lattice mismatch to the ZnO lattice, i.e. gallium nitride template (GaN/Al_2O_3), sapphire, silicon carbide and zinc oxide single crystal. The mismatch between ZnO and GaN is only 1.9%. Therefore, we expected lower stress and dislocations density. The lattice mismatch for SiC and Al_2O_3 substrates is higher and equals 5.4% and 31.7%, respectively. In the latter case the actual lattice mismatch is reduced to 18.4% by rotation of the ZnO unit cell of growing ZnO layers with respect to the substrate unit cell by 30° [11].

The ALD process consists of repeating four deposition steps: deposition of a first precursor; purging the reaction chamber with an inert gas, when non-reacted precursors' and by-products' molecules are removed; deposition of a second precursor; and final purging of the reaction chamber. Thus several parameters affect final quality of ZnO films. These are lengths of pulses, growth temperature, purging times, etc. Moreover, the crystallographic quality of the ZnO-ALD film as well the surface morphology depends on the kind of precursors used. We found that when using DEZn and water for the ZnO deposition a long purging time and higher growth temperature are advantageous. The growth with c axis perpendicular to the surface is achieved at these conditions. In this case only the 00.2 peak is observed in the XRD spectrum. In the following experiments we used ALD parameters that are feverous for ZnO growth with c axis perpendicular to the surface. Deposition temperature was 300 °C. The same conditions were used for the ALD processes in all investigated substrates.

In Fig. 1 SEM images are shown of ZnO/SiC, ZnO/ZnO, ZnO/Si and ZnO/GaN interfaces. For the silicon substrate, where the lattice mismatch is very high (about 40%) the monocrystalline growth was not achieved. One can see here a columnar growth with a column width about 100 nm. A columnar growth was less evident in case of ZnO/GaN and ZnO/SiC films, which are of much higher structural quality. We observed that some dislocations coming from the gallium nitride and silicon carbide substrates are spreading into the zinc oxide layer. From the SEM images and epitaxy software calculations (PANAlytical software used for plotting and analyzing rocking curves, 2-axes scans, reciprocal space) one can conclude that zinc oxide films are fully relaxed. An ideal interface and the best ZnO layer quality are obtained for the homoepitaxial growth i.e., for ZnO/ZnO process. In this case the zinc oxide film is fully uniform and neither dislocations nor grain boundaries are seen in the SEM image.

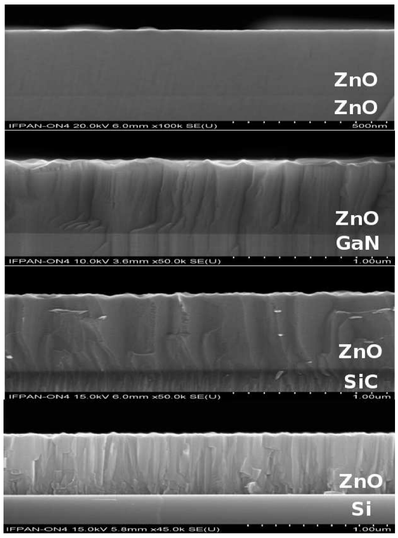

Fig. 1. SEM studies show good structural quality of ZnO films deposited on different substrates. The best monocrystalline quality was obtained for zinc oxide and gallium nitride substrates.

Figure 2 shows reciprocal space maps (RSM) of the 00.2 reflection from the epitaxial ZnO films deposited on GaN, SiC, Al_2O_3 and ZnO. The RSM maps confirm that ZnO layers obtained are monocrystalline, with a full width at half maximum (FWHM) of the rocking curve (00.2 reflection) equal to 0.009° and 0.058° for ZnO/ZnO and ZnO/GaN, respectively. The reason of rather high diffuse scattering (elliptical shape isocontures with 3 ordered smaller intensity than for the Bragg peak) is different for these two substrates. Films grown on GaN templates reflect the structural imperfection of the templates (GaN/sapphire; dislocation density in order of the 10^9 cm^{-2}). Ellipses visible in Fig. 2b are twice more elongated in Q_x direction than for the ZnO/ZnO case (Fig. 2c). We suppose that diffuse scattering for homoepitaxial growth of ZnO is correlated with the surface imperfection. For ZnO/Al_2O_3 and ZnO/SiC the FWHM

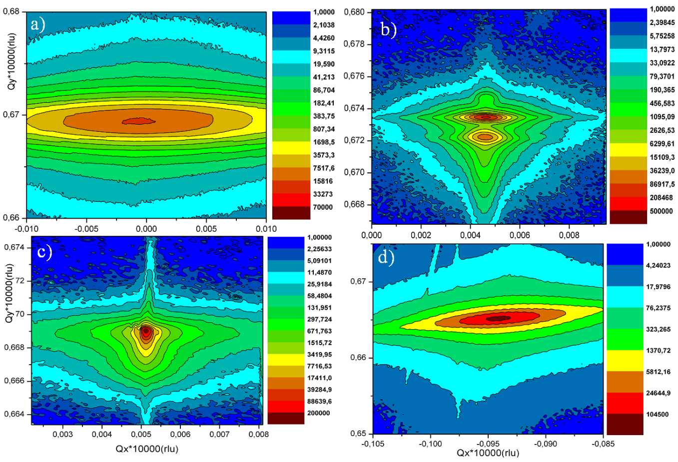

Fig. 2. Reciprocal space maps of the 00.2 reflection from zinc oxide deposited on (a) sapphire, (b) gallium nitride, (c) zinc oxide bulk crystal, (d) silicon carbide.

of the rocking curve is equal to 0.991° and 0.345°, respectively.

The lattice parameters of the obtained films were determined from the RSMs of symmetrical 00.2 and the asymmetrical −1−1.4 reflections. In Table we present the lattice parameters of ZnO. The data for films deposited on different substrates are compared with single crystal lattice parameters of ZnO [12]. One can see that lattice constants of ZnO-ALD films are very similar to these of a single ZnO crystal. For ZnO/ZnO homoepitaxial films the differences between lattice parameters of bulk and epitaxial ZnO are within the error limit. Surprisingly, the values of lattice parameters for the ZnO layer grown on sapphire are only about 0.02% larger than these of a ZnO single crystal. However, the higher FWHM of the 00.2 peak for ZnO films deposited on Al_2O_3 suggests a higher screw dislocation density. The largest differences in lattice parameters are noticed for ZnO films deposited on GaN and SiC substrates. For ZnO/GaN a and c lattice constants are 1.1% larger and 1.6% smaller than lattice constants of a zinc oxide single crystal. This shows that the layer deposited on gallium nitride is tensile strained in the (0001) plane. A similar situation is observed for the ZnO/SiC film. The optical properties of epitaxial ZnO films were characterized by RT and LT PL.

Figure 3 shows RT PL spectra of zinc oxide deposited on Al_2O_3, GaN and ZnO single crystal. We observed here high edge luminescence in the blue spectral region. Defect-related PL usually observed as a broad band in the visible spectral region is not present in any measured films. The spectral position of the edge emission is similar for all investigated ZnO layers and is 3.25 eV. The strongest edge luminescence is observed for ZnO films grown on a sapphire substrate. It is probably related to the full relaxation of ZnO/Al_2O_3 films which was postulated above. PL spectra measured at 12 K are presented in Fig. 4. PL shows sharp excitonic luminescence with

TABLE

Lattice constants parameters for zinc oxide thin films deposited on zinc oxide single crystal, gallium nitride, sapphire, silicon carbide. The lattice constant of zinc oxide single crystal are a = 3.2495 Å and c = 5.2069 Å [9].

Substrates	Lattice a [Å]	Lattice c [Å]
GaN	3.2534	5.1986
SiC (4H)	3.2513	5.1957
Al_2O_3	3.2488	5.2057
ZnO	3.2492	5.2067

FWHM values of 4 meV, 5 meV and 6 meV for ZnO/GaN, ZnO/ZnO and ZnO/Al_2O_3, respectively. In PL spectrum of zinc oxide deposited on sapphire we observe two peaks: higher one at 3.36 eV corresponding to neutral donor-bound exciton recombination [13], and a smaller peak at 3.33 eV likely also corresponding to a donor-bound exciton transition [14]. The same peaks are seen for zinc oxide deposited on the gallium nitride substrate, but with different intensities. Donor-bound excitonic emission at 3.33 eV is dominant in the ZnO/GaN spectrum. For ZnO obtained on gallium nitride we notice phonon replied of the PL peaks. This confirms the good crystallographic quality of the films studied. Homoepitaxial zinc oxide layers show much weaker low-temperature photoluminescence. We attribute this to a diffusion of lithium and/or potassium contaminations from the commercial zinc oxide substrate to ZnO layers. Our films were grown on substrates obtained by hydrothermal method which contain large Li and K concentration.

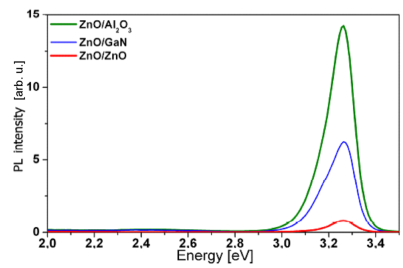

Fig. 3. Room temperature photoluminescence for zinc oxide thin films deposited on gallium nitride, single crystal zinc oxide and sapphire.

We note here that structural and optical parameters shown above are comparable with the ones reported for epitaxial ZnO films obtained at much higher temperatures by CVD or MBE [15]. For example, ZnO grown on GaN substrate by CVD at 700 °C shows the rocking curve of 1000 arcsec [15], which is much higher than for our ZnO/GaN films (250 arcsec).

The electrical parameters of ZnO/GaN and ZnO/Al_2O_3 have been examined by the Hall effect measurements. These investigations were performed at room

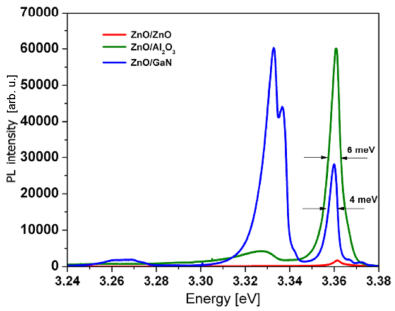

Fig. 4. Low temperature photoluminescence for zinc oxide thin films deposited on gallium nitride substrate, single crystal zinc oxide and sapphire.

temperature in the van der Pauw configuration using the RH2035 PhysTech GmbH system equipped with a permanent magnet giving a field of 0.426 T. The free carrier concentration was 1.8×10^{18} cm^{-3} for a ZnO/GaN film and 2.2×10^{18} cm^{-3} for a ZnO/Al_2O_3 layer. These values are about one order of magnitude lower than obtained for a ZnO film deposited on a glass substrate in the same ALD process, where the ZnO layer was polycrystalline. For ZnO/glass films we obtained n concentration of 1.3×10^{19} cm^{-3}. The measured mobility of carriers was higher for epitaxial layers than for the polycrystalline films. The mobility is also strongly correlated with the structural quality of the film. The mobility μ for ZnO/GaN film (the FWHM of the rocking curve 250 arcsec) was 167 cm^2/(V s), whereas μ for ZnO/Al_2O_3 layer (the FWHM of the rocking curve 3560 arcsec) equals 39 cm^2/(V s). For comparison, the mobility of carriers in the reference polycrystalline ZnO/glass film is about 30 cm^2/(V s).

4. Conclusions

In conclusion, we obtained monocrystalline ZnO films on GaN and bulk ZnO substrates by atomic layer deposition at temperature 300 °C. The structural and optical parameters "as-grown" ZnO films are surprisingly good despite low growth temperature. We note here that structural and optical parameters shown above are comparable with the ones reported for epitaxial ZnO films obtained at much higher temperatures by CVD or MBE. For example, ZnO grown on GaN substrate by CVD at 700 °C shows the rocking curve of 1000 arcsec, which is much higher than for our ZnO/GaN films (250 arcsec). Electrical properties of epitaxial ZnO films strongly correlate with the FWHM of the rocking curve. For ZnO/GaN films mobility of carriers is a 169 cm^2/(V s) and free electron concentration at RT is 1.8×10^{18} cm^{-3}. All these parameters favorably compare with the ones obtained at higher temperature with MBE or MOCVD.

Acknowledgments

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