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NANOSCOPIC STUDY OF ZnO FILMS BY ELECTRON BEAM INDUCED CURRENT IN THE SCANNING TUNNELING MICROSCOPE

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Scanning tunnelling microscopy and spectroscopy have been used to characterize electrically active grain boundaries in pulsed laser deposited ZnO films with grain sizes in the range 216-500 nm. The p-type behaviour at the boundary is evidenced by local STM conductance spectra, which reveal boundaries with a n-p-i-p-n structure. In addition, local differential conductance measurements show higher surface band gap at the grain boundaries than in the grain interior, which is related to the space charge at the boundaries. The beam induced current mode of the STM has been used to image electrically active grain boundaries with a resolution of few nanometers in the different films. It is demonstrated that in some of the small grains the space charge region extends to the whole grain area so that no electrical barrier can be related to the grain boundary.

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1. Introduction

Several wide band gap semiconductors, as GaN and SiC, have been intensively investigated in the past years because of their important applications as short wavelength photonic devices or in the field of high power electronics. More recently, ZnO has been increasingly considered for similar applications as the mentioned materials, and methods for large area single crystals growth as well as epitaxial layers growth have been developed or improved. In particular, pulsed laser deposition (PLD) which has become an outstanding technique in the preparation of thin films, especially oxides, has been used to obtain high quality ZnO films e.g. Refs. [1,2]. In the case of ZnO films grown on (100) InP by PLD a strong dependence of grain size and morphology, and in general of crystalline quality, on the film thickness has been observed [3,4]. The grain size ranges from some nanometers for film thickness below 200 nm to sub-micron structures above this thickness. The influence of grain boundaries and other defects, on electrical and optical properties of bulk ZnO ceramics, has been investigated in the past by different spatially resolved techniques as electron beam induced current (EBIC) or cathodoluminescence (CL) in the scanning electron microscope (SEM), as well as scanning tunnelling microscopy (STM). Such studies have demonstrated the complex nature of grain boundaries, which are electrically active regions with an associated space charge and specific recombination properties. Some of the electrical properties of conducting ceramics have been often related to the presence of space charges and the associated built-in fields at the grain boundaries which are considered to form a n-i-n barrier structure. One of the techniques with spatial resolution which has been used to study electrical barriers in ZnO and high resistivity polycrystalline semiconductors is remote electron beam induced current (REBIC) in the SEM [5,6,7,8] whose resolution is normally of the order of a fraction of a micron. The mentioned SEM-based techniques,

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with typical spatial resolution in the micron-submicron range, are not suitable to characterize samples with grain size, or other features, in the order of tens or few hundreds of nanometers. On the other hand, high resolution electrical characterization of such samples can be performed with scanning probe techniques. In particular, scanning tunnelling spectroscopy and microscopy have been used to characterize ZnO polycrystals, e.g. [9,10,11] and single crystals [12,13] while beam induced current in the STM, which is analogous to the beam induced current methods widely used in SEM, was employed to image electrically active grain boundaries in ZnO ceramics [14]. In the present work local electrical properties of PLD ZnO films with different grain sizes, have been characterized by STM, STS and the remote beam induced current technique in the STM (STM-REBIC).

2. Experimental

ZnO films were prepared by PLD by using a KrF excimer laser with pulse width and repetition rate of 16 ns and 10 Hz respectively. The deposition was carried out in a high vacuum chamber with a pressure of $8x10^{-7}$ mbar on a (100) InP single crystal substrate at 350 ºC. Details on the growth conditions are described in ref.4. The grain size of the obtained films depends on the number of pulses, or the film thickness. The investigated samples had grain sizes of 218 nm and 550 nm respectively with thicknesses from 250 nm to 1.4 μm. The microscopy measurements were performed in a combined SEM-STM instrument based on a Leica 440 SEM operating under a vacuum of 10^{-6} torr. The main features of the instrument are similar to those previously described in ref. [15]. The STM was used in the conventional constant-current mode, in the current imaging tunnelling spectroscopy (CITS) mode and in the STM-REBIC mode. CITS provides real space imaging of surface electronic states by recording I-V curves at fixed tip-sample separation at every pixel within an image [16,17]. In addition to the I-V curves, current images can be formed by plotting the measured current at any voltage. The data are represented by using the ratio of differential to total conductance (dI/dV)/(I/V), which gives a rather direct measure of the surface density of states [18,19]. The contact arrangement for STM-REBIC was similar to that described in ref. [20], which is the tunnel equivalent of the SEM-REBIC configuration. The two ohmic contacts, separated about 2-3 mm were provided by silver paste and gold wires. The tunnel tip was located above the region between the contacts.

3. Results and discussion

Local differential conductance measurements were performed in different grains and boundaries of the investigated samples. The results obtained for the surface band gap in the different grains or regions of a grain, as measured from the conductance spectra, show a high dispersion of values. The samples showed in general a wider band gap in the boundaries than inside the grains. The band gap at the boundaries is about 2.4 eV, while inside the grains has a value of 0.6 eV approximately. The CITS images also reveal the different electronic behaviour of grains and grain boundaries (Fig. 1). As stated above, this effect is due to the space charges and associated built-in fields at the boundary that have been used to explain the varistor non-linear effect of ZnO ceramics [20]. Previous works on spatially resolved tunneling spectroscopy of ZnO ceramics have shown different widths of the zero conductivity region in the conductance spectra [10,11,14]. In the case of undoped bulk ZnO ceramics the observed band gap is lower at the boundaries than inside the grains [14], which is opposite to the present observations, while in varistor ceramics similar values to those obtained in this work are observed [10]. This shows that the presence of the doping species, oxides in the case of varistors, in the ceramics do not determine the difference in the value of zero conductivity between boundaries and grains.

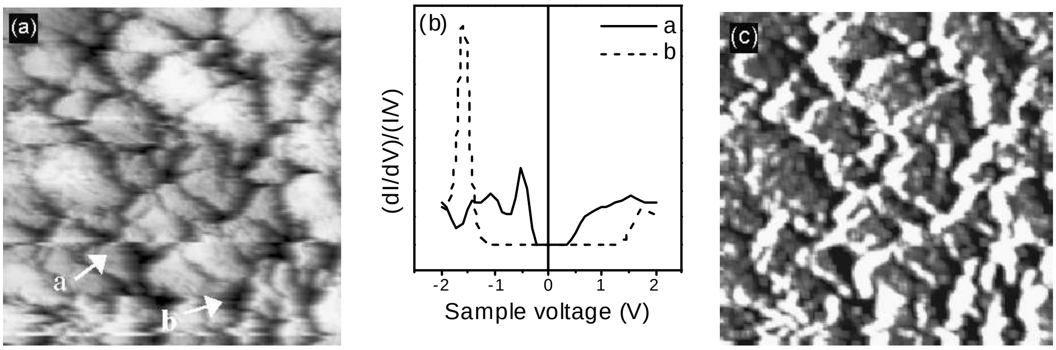


Fig. 1. a) 1.2×1.2 μm^2 STM constant current image of the sample of 218 nm grain size acquired with -1.8V sample bias and 0.5 nA tunnelling current. b) Normalized differential conductance spectra from areas a and b marked in part (a). c) CITS image of the same area acquired at –2.0V.

The presence of space charge regions at the boundaries is also detected, with high spatial resolution, by STM-REBIC. This technique has been only occasionally used to image defects in high resistivity semiconductors or ceramic materials as $CuInSe_2$ [21], diamond [22] or bulk sintered zinc oxide [14], however it has not been, to our knowledge, applied to characterize ZnO nanocrystalline films. Fig. 2 shows the constant current image of a region of the film with average grain size of 550 nm and the corresponding STM-REBIC image of the same area. The REBIC contrast is mainly related to the grain boundaries and appears as a bright zone at one side of the boundary. The size of some features resolved in this image, as the width of the boundary, is about 3-4 nanometers. Fig. 3 shows STM and STM-REBIC images of the sample with average grain size of 218 nm. In this case not only some boundaries but also some regions, which correspond to small grains, show bright REBIC contrast. This effect could be due to a large width (about 70nm at each side of the boundary) of the space charge region at the boundary in some of the smaller grains. The influence of the boundary in these cases practically extends to the whole grain volume so that no electrical barriers can be related to the boundary.

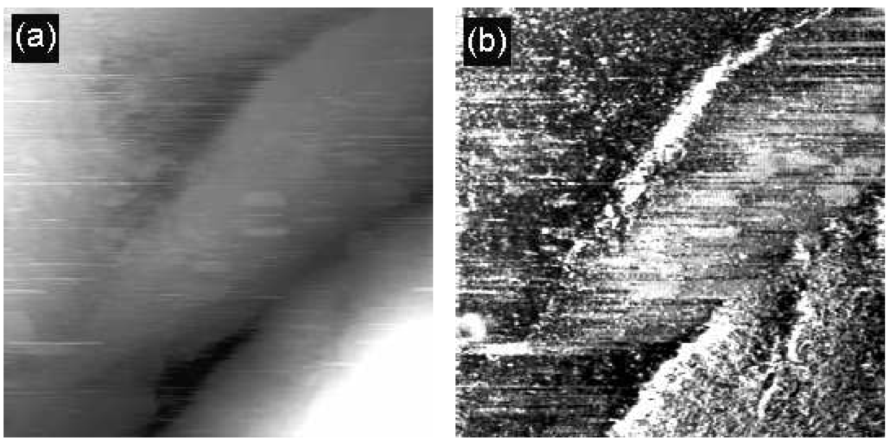


Fig. 2. a) 170×170 nm^2 STM constant current image of the sample of 550 nm grain size. b) STM-REBIC image of the area shown in (a).

The resolution in the present STM-REBIC images is similar to that reported in the previous STM-REBIC works mentioned above, and higher than the typically attainable resolution in SEM - REBIC measurements.

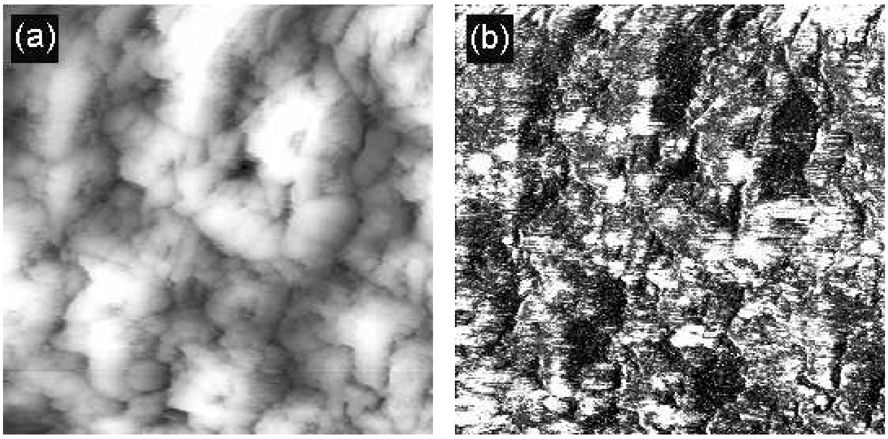


Fig. 3. a) 1x1 μm^2 STM constant current image of the sample of 218 nm grain size acquired with 2V tip bias and 4 nA tunnelling current. b) STM-REBIC image of the area shown in (a).

The STM-REBIC images show that not all the boundaries are imaged or present similar contrast which indicates that not all of them have the same electrical activity. Typical reported SEM-REBIC contrast of the boundary consists of a black-white region extending at both sides of the boundary, usually referred as peak and trough (PAT) contrast which is explained by modelling the boundary as two back-to-back Schottky barriers, e.g. Ref. 8. Although the REBIC contrast in SEM and STM cannot be directly compared due to the different excitation conditions and the surface related nature of the STM measurements, we have also observed in some cases the PAT contrast (Fig. 4).

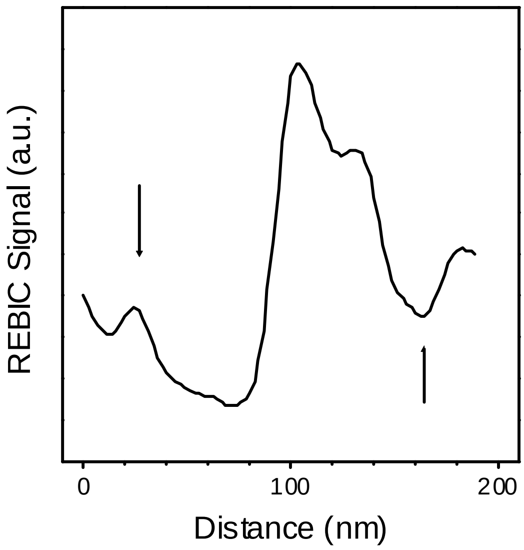
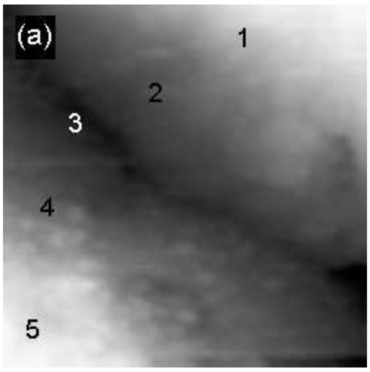


Fig. 4. Typical REBIC profile acquired on 550 nm grain size sample. Arrows mark the limits of the space charged region at both sides of the boundaries.

The model of a grain boundary as two Schottky barriers is demonstrated by local conductance measurements across the boundary. Fig. 5 shows the STM constant current image of a boundary and a series of conductance spectra recorded across it. These spectra demonstrate the appearance of a n-p-i-p-n space layer which corresponds to the back-to-back Schottky barrier structure.



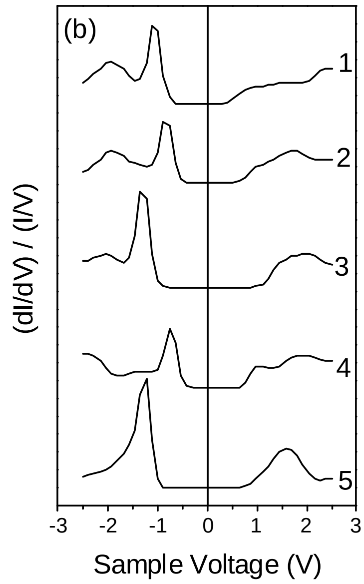


Fig. 5. a) 90×90 nm^2 STM constant current image of the sample of 550 nm grain size acquired with -1.8 V sample voltage and 0.2nA tunnelling current. b) Normalized differential conductance spectra from points 1 to 5 marked on part (a).

4. Conclusions

STM-REBIC mapping of ZnO films enables to image, with a resolution of few nanometers, electrically active boundaries and space charge regions. Some boundaries show the PAT contrast of the boundary corresponding to a back-to-back Schottky barrier structure. Differential conductance measurements across a boundary confirm the n-p-i-p-n electrical structure. STM-REBIC also shows bright contrast of small grains which is attributed to the long range of the space charge which extends into the whole grain. STS and CITS show different conductance behaviour at the grain boundaries than in grain interior. The grains may present different types of conductivity while boundaries are always p-type, which is due to the existence of the space charge region at the boundary. The band gap is wider at the boundaries as compared to the grain interiors.

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