Strain effects in ZnO layers deposited on 6H-SiC

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Correlation in crystallite sizes and defects of epitaxial ZnO layers deposited on 6H-SiC substrates has been addressed. The biaxial strain governs the ZnO crystallites for the layer thickness of ~ 400 nm. The misfit dislocations were observed in nucleation and theater is the columnar growth mode diffracted in transmission electron microscopy. The columnar growth mode is a symbol of stacking faults that appear due to imbalanced interface chemistry in the II-VI/IV materials system, together with the complex impurity matrix. These defects are the main source of nonradiative recombination centers in ZnO epitaxy resulting in shorter exciton lifetimes examined in time-resolved photoluminescence measurements. © 2006 American Institute of Physics.

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I. INTRODUCTION

An explosive expansion of research onto ZnO and related oxide materials (MgO and CdO) has continued for the fabrication of blue to ultraviolet light emitting diodes (LEDs) and exciton- and polariton-based laser diodes (LDs) since the exciton and biexciton binding energies of bulk ZnO are 60 and 15 meV, respectively.¹ With the higher oscillator strength associated with the excitons and biexcitons, these features could lead to a lower-threshold lasing, higher quantum efficiencies, and faster optical device switching. It is expected that these promising features of epitaxial ZnO layer will contribute directly to the optoelectronic and nanoelectronic devices operated at elevated temperatures. In addition, the higher cohesive energy and melting point of ZnO material indicate the strong bond strength, suggesting that the degradation of devices during operation might not be an issue.

A number of studies have been performed on ZnO epitaxy where strain plays the main driving force for crystallinity.^{2,3} In ZnO/6H-SiC heteroepitaxy, the stress induced by the lattice misfits of $\sim 5\%$ is fully relaxed when the film thickness becomes larger than the several nanometers of critical thickness.^{4,5} It has been demonstrated that the strain relaxation is affected by growth conditions, VI/II molar ratios, and layer thickness, and it is also adhered that the structural and optical properties are strongly correlated with the degrees of the strain. For an example, the threshold power density in stimulated emission decreases with an increase of the strain.⁶ We have demonstrated the nucleation and inter-

face chemistry of ZnO deposited on SiC substrate.^{4,5} However, the main driving force for biaxial strain in the ZnO/SiC heterostructure is yet to be addressed.

In this paper, the degree of strain relaxation and strain-induced defects in ZnO layers deposited on SiC substrates have been addressed experimentally and assessed theoretically. The growth mode switching from islands to grains critically depends on the accommodated strain due to increase of crystallite sizes. Crystallites are diffracted in transmission electron microscopy with the columnar growth mode; a symbol of stacking faults appears for the imbalanced interface chemistry, together with the complex impurity matrix. These results suggest that the strain relaxation process is associated with defects which act as nonradiative recombination centers, together with the band gap energy shifting.

II. EXPERIMENTS

ZnO layers were deposited on 6H-SiC(0001) substrates by metal organic chemical-vapor deposition. The details of chemical cleaning and processing have been discussed elsewhere.^{4,5} Prior to ZnO deposition, the diethyl zinc (DEZn) was flowed first for 40–80 s and then O₂ was flowed. The flow rate of DEZn was kept to 6 SCCM, while the O₂ flow rate was 10 SCCM (SCCM denotes cubic centimeter per minute at STP). For ZnO deposition, the flow rate of DEZn was controlled by adjusting the flow rate of carrier gas N₂. The substrate temperature was then increased to the selective growth temperature of 475 °C for the successive growth of ZnO layers on the SiC. To avoid thickness fluctuation error, each sample was carefully calibrated and instrumental error was recorded on an average to be $\pm(1-3)$ nm.

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FIG. 1. [(a)–(c)] The AFM images of ZnO deposited on SiC substrates. The island growth mode switches to the grain growth modes due to increase of layer thickness. (d) The crystallite sizes are plotted as a function of layer thickness. (e) Strain along the c axis due to crystallite size. (f) Strain along the a and c axes lengths as a function of a axis and c axis lengths, respectively.

The c axis and a axis lengths of ZnO layers were determined by x-ray diffraction (XRD) using the triple-axis ω - 2θ scans on the (002) and (205) reflections, respectively. Two orthogonal $[11\bar{2}0]$ and $[10\bar{1}0]$ cross-section specimens were prepared for transmission electron microscopy (TEM) examination using the standard procedures and thinned by Ar^+ ion milling. The microscopy was performed using a JEOL 200CX operated at 200 kV and a JEOL 4000EX operated at 300 kV. Time-resolved photoluminescence (TRPL) measurements were performed by a frequency-tripled mode-locked Ti:sapphire laser, with a standard streak-camera acquisition technique at 293 K.

III. RESULTS AND DISCUSSION

Figures 1(a)–1(c) show the partial and/or complete coverage of ZnO deposited on SiC substrates assessed in contact-mode atomic force microscopy (AFM). For the ZnO layer thickness of ≤ 2 nm, a partial coverage of ZnO islands with the substrate background is visible in Fig. 1(a). With the increase of ZnO layer thickness, however, each island makes contact with its neighbors giving rise to coalescence and finally to the grain morphology, as shown in Figs. 1(b) and 1(c). Presumably, these are the three-dimensional (3D) columnar grains typically observed in the various thin films.^{7,8}

This paradigm is embodied in the nanoheteroepitaxy approach where the strain energy is reduced by leveraging the high, 3D compliance of nanoscale features.⁹

These nanocrystallite sizes were assessed by AFM section analysis due to ZnO layer thickness plotted in Fig. 1(d). The aspect ratios (height/width) of these crystallites increase slowly with the increase of ZnO layer thickness. The crystallite sizes, however, became independent for the layer thickness of ~ 400 nm. This indicates that the growth modes are independent after the relaxation of biaxial strain by leading to the 3D grain morphology. In principle, the misfit dislocations (MDs) and related defects occur while the growth mode transforms from two-dimensional (2D) islands to 3D grains.¹⁰ It is noted that the growth geometry of ZnO/SiC heterostructure is satisfied by this rule since the lattice mismatch is $\sim 5\%$.⁴

Correlation in strain and crystallite size has been plotted in Fig. 1(e). It is noteworthy that the strain energy in the nucleation is very large, -2.4% , indicating that the islands are grown under the strain energy on SiC, mostly due to the layer/substrate misfits. The biaxial strain, however, decreases drastically with the increase of ZnO crystallite sizes and gradually relieves afterwards. It has been demonstrated that the strain energy also critically depends on the layer thickness, and relieves $\sim 94\%$ at the larger grain sizes for the ZnO layer thickness of $1.5 \mu\text{m}$.⁴ This correlation among the growth modes, crystallite size, and strain kinetics discloses a clear role reflected in Figs. 1(a)–1(c) as a function of crystallite size. The large lattice mismatch ($\Delta a/a \approx \sim 5\%$), therefore, in the ZnO/SiC heterostructure is seen as the driving force which induces the 2D-3D change of the surface morphology by the formation of grains.

Figure 1(f) shows the lattice parameters a and c versus strain parallel and perpendicular to the plane of ZnO layers grown on SiC substrates. These structural parameters were evaluated using the four-axis x-ray diffraction measurements and details of these results have been reported elsewhere.^{4,5} The plotted results exhibit the linear relationship between the lattice parameters and the epitaxial layers deformed elastically by stress in the epilayers. The a axis length is almost linear with respect to the strain along the c axis due to the increase of layer thickness, but the c axis length relaxes faster than the a axis length for the thick layers. This anomaly in the lattice parameters is the result of biaxial strain kinetics since the ZnO belongs to the space group $P_63mc=C_{6v}^4$ in which, in principle, the materials grow along the c axis and relax faster perpendicular to the substrate.

The strain kinetics has been assessed theoretically by considering the MD at the heterointerfaces. The energy cost E_{MD} required for creating a unit length MD at the heterointerface is given by

$$E_{\text{MD}} = \frac{\ln(1 + h/b) \mu b^2 (1 - \nu/4)}{4\pi(1 - \nu)}, \quad (1)$$

where μ is the shear modulus at the interface between the film and the substrate [μ is equal to $(C_{11} - C_{12} + C_{44})/3$] for the slip system $\langle 011 \rangle \{111\}$, h is the layer thickness, ν is the Poisson ratio, and b is the Burgers vector. Figure 2(a) shows the E_{MD} as a function of ZnO layer thickness deposited on

FIG. 2. (a) Theoretical interpretation of misfit dislocation energy E_{MD} as a function of layer thickness. (b) Plot of lattice mismatch kinetics due to the ZnO layer thickness grown on SiC substrates.

SiC substrate. For comparison, ZnO/Al₂O₃ and GaN/SiC heterostructures have been fitted theoretically and plotted in Fig. 2(a) using the standard parameters. The parameters used in this fitting were $b=2.253$, the absolute lattice constant of ZnO, and $\mu=1$. It is found that the MDs are easier to form in the ZnO/SiC heterostructure than in the ZnO/Al₂O₃ and GaN/SiC materials systems. It has been demonstrated that the MDs are really easier to form in II-VI than in III-V, which is a major clue for understanding why, at misfit as large as 6%, systems such as InAs/GaAs exhibit a SK transition whereas others, such as CdTe/ZnTe or CdSe/ZnSe, do not.¹⁰ This corresponds to a plastic relaxation considered by Frank and van der Merwe. On the other hand, there are systems such as GaN/AlN (Ref. 11) or SiGe/Si,^{12,13} with lower misfit (respectively, 2.4% and less than 4%), which are known for exhibiting a clear SK transition with the formation of coherent islands.

This has been assessed experimentally by calculating the lattice mismatch of ZnO/SiC heterostructure as a function of layer thickness, plotted in Fig. 2(b). The lattice mismatch by the misfit parameter δ is defined by $\delta=(a_{\text{sub}}-a)/a_{\text{sub}} \times 100\%$. The lattice relaxation due to increase of the layer thickness can be addressed by four sections marked as 1, 2, 3, and 4 in Fig. 2(b). The lattice mismatch relaxation starts for the layer thickness of ~ 6 nm and then remains constant in strain for a fluctuation of 0.10%. However, it relaxes faster for the layer thickness of 6 nm and suddenly slows down in

FIG. 3. (a) TEM cross-section of ZnO/SiC heterostructure where columnar growth mode is evident. (b) Sketch of the possible imbalanced interface chemistry. The As or related materials may satisfy the misbalancing problem in the II-VI/IV materials system.

the layer thickness of 80–380 nm, in good analogy to crystallite size in AFM observation. This overall experimental evidence, therefore, is in good agreement with theory, which is plotted in Fig. 2(b) by a solid line. If the misfit parameter δ and thickness h of the epilayer are small, the misfit between the two semiconductors is accommodated by the trigonal strain in the epilayer. For a given δ if thickness h of the epilayer exceeds a certain thickness, known as critical thickness h_c , the strain is partly accommodated by the misfit dislocations ($\epsilon_{||} = -\delta$). If the lattice constant of the layer is smaller than that of the substrate, δ is negative, the strain is tensile, and ϵ is positive. According to this convention, tensile strain and stress are positive and compressive strain and stress are negative. The fluctuating part has an average of zero and therefore does not interact with the homogeneous strains. Using all of these contributions, the expression for the total energy E_T^m (per unit area) of the uncapped layer can be written as

$$E_T^m = E_H^{\text{AD}} + \frac{2}{p} \frac{\mu b^2}{4\pi(1-\nu)} \left[(1 - \nu \cos^2 \beta) \ln \frac{\rho_c h}{q} \right], \quad (2)$$

where E_H is the energy corresponding to misfit strain, dislocation arrays, and interaction between the average strain due to dislocation arrays (AD) and the homogeneous misfit strain, and the second part is the energy E_{DS} due to the fluctuating part of the strain of dislocation arrays—for a single isolated dislocation given by $E_{\text{DS}}^{\infty} = \mu b^2 / 4\pi(1-\nu) [(1 - \nu \cos^2 \beta) \ln(\rho_c h/q)]$. Here ρ_c is a parameter introduced to account for the nonelastic part of the core energy of the dislocations and q is the core radius of the dislocation line, usually taken to be equal to b . We have used $\rho_c = 1$, $\nu = 0.36$, and $\mu = 1$ in the calculations presented in this article. The fitted results are $p = -2945$ and $E_H = 0.224$, in good agreement with the experiment.

High-resolution TEM cross section of ZnO/SiC heterostructure is represented in Fig. 3(a). The cross section exhib-

FIG. 4. A typical TRPL of ZnO layer deposited on SiC substrate taken at room temperature. The inset shows the TRPL image taken from the sample at room temperature.

its the columnar growth mode with dislocations in the heterointerface, as expected for the larger lattice and thermal misfits in the ZnO/SiC heteroepitaxy. The average lateral domain sizes are on the order of 100 nm. The clear dark line almost along the c axis in the ZnO layer represents a threading dislocation. The threading dislocation does not significantly affect the growth of ZnO on it. A close look at the image reveals that near the ZnO surface, smaller domains of a few tens of nanometers in width exist. Such smaller-domain structures extend for around 100 nm along the growth direction, after which the larger-domain structures at the size order of 100 nm are formed by connecting smaller domains. The columnar growth mode has been subjected to the imbalance of interface chemistry in the II-VI/IV materials system.

Clearly visible stacking faults in the ZnO epilayer may be responsible for the imbalanced charge distribution in the II-VI/IV materials system. For the ZnO/SiC system, the imbalanced charge distribution can be understood in terms of ZnO in the following electron counting argument sketched in Fig. 3(b): in the ZnO, each Zn (O) atom contributes 1/2 (3/2) electron to each of the four bonds surrounding it, and in bulk Si, each atom contributes exactly one electron per bond. At a (0001) interface between the Si and Zn of ZnO, therefore, the interface bonds with each reach a total of 3/2 electrons instead of the two electrons required. Therefore, the imbalanced electron distribution and dangling atomic bonds are responsible for the columnar growth modes and related defects. It also diffracts that the SiC substrate surface contains nanoscale fluctuations and scratches, which played an important role in the formation of defects in ZnO epilayers.

To compare the nonradiative defect density, TRPL signals of free excitonic emission peaks in the ZnO epilayers were excited by a frequency-tripled mode-locked Ti:sapphire laser. TRPL signals of ZnO layers deposited on SiC substrates monitored at particular photon energies at room temperature (RT) are summarized in Fig. 4. The TRPL decay spectra can be well fitted using a biexponential line shape $I(t) = I_1 \exp(-t/\tau_R) + I_2 \exp(-t/\tau_{\text{NR}})$, where $I(t)$ is the PL intensity at time t and I_1 represents the initial intensity of the i th component. The fast decay constant (τ_R) probably represents the effective radiative lifetime of localized excitons of

450 ps. On the other hand, the slow one (τ_{NR}) is too long to be accounted for in any intrinsic radiative process. The longer time constants in the two-exponential fits can be attributed to the radiative lifetime of the exciton, although the origin of the short-time constant is not certain. Two possibilities may be invoked for the nonradiative processes in origin: defect concentration changes over the sample in such a way that the concentration increases linearly over the growth time and surface states cause nonnonradiative decay. It is added that the optical band structure of ZnO/SiC heterostructures was modified considerably by the biaxial strain incorporated due to the lattice and thermal misfits.¹⁴ In principle, the c/a ratio reduction counteracts the increase and/or fluctuations in the optical bands due to the volume compression.¹⁴

In this experiment, C, Si, N, and Al impurities were dominant in the ZnO epitaxy, while O and Al are incorporated in the SiC substrate.^{4,5} It is evident that the O concentration in the interface is lower than the bulk SiC which is in analogy discussed in substrate surface preparation. Therefore, it is expected that these defects extended in the ZnO due to the complex impurity matrix contributed/interdiffused from the host ZnO material, SiC substrate, and metal organic precursors. Although the defect generation possibility in ZnO/SiC heterostructure is rather higher than that in ZnO/Al₂O₃ theoretically, experimentally, defect concentration might be low, which is reflected in the high-quality ZnO epilayers deposited on SiC substrates. From these experimental evidences, therefore, it is addressed that the biaxial strain, together with the complex impurity matrix, controls the crystalline quality of epitaxial ZnO layers deposited on SiC substrates.

IV. CONCLUSIONS

In this paper, strain-induced defects and their effects on structural and optical properties in ZnO epitaxial layers de-

posited on SiC substrates have been demonstrated. The biaxial strain in ZnO/SiC heterostructure is the main driving force for generation of defects, together with impurities and imbalanced interfaces. The columnar growth is the result of the imbalanced heterointerfaces that were observed in TEM, which are responsible for shorter exciton lifetime.

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