ZnO growth on Si substrates by metalorganic vapor phase epitaxy

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Abstract

Diethylzinc (DEZn) and nitrous oxide (N\textsubscript{2}O) as a source gas combination in the metalorganic vapor phase epitaxy (MOVPE) of zinc oxide (ZnO) has produced high-quality layers on sapphire, but no growth was confirmed on Si. This problem was overcome by using an underlying layer of ZnO grown directly onto the Si using nitrogen oxide (NO\textsubscript{2}) as a more reactive oxidation source. The main ZnO layer grown in this way on the ZnO/Si pretreated at 800°C possessed a c-axis orientation and exhibited bound exciton (BX) emission as narrow as 3 meV at full-width at half-maximum together with a free exciton (EX) at 9 K. These results demonstrated the high potential of MOVPE technology for the growth of ZnO on Si using appropriate surface treatments for optical and electrical applications.

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1. Introduction

Much interest in ZnO is developing following the concept of novel devices using excitonic effects as well as those using its multi-functional properties. Recently, our results on ZnO grown on sapphire by metalorganic vapor phase epitaxy (MOVPE) using diethylzinc (DEZn) and nitrous oxide (N\textsubscript{2}O) have shown its strong photoluminescence (PL) from free excitons at RT and sharp excitonic emission as narrow as 3 meV at full-width at half-maximum (FWHM) at 15 K [1,2], which demonstrated the MOVPE growth of high-quality ZnO. Compared with previous [3] and recent [4] results, this success should be attributed not only to the technical advantages of MOVPE such as its suitability for the growth of the compounds which contain volatile elements, but also to the progress of II–VI MOVPE technology and to the purity of the source materials [5,6] achieved during a lot of research work on ZnSe-based semiconductors for blue–green laser diodes.
From the viewpoint of hybridization with LSI-based structures of Si, ZnO growth on Si is of much interest. Moreover, the availability of large high-quality Si substrates, as well as their low cost, make it an attractive alternative substrate to sapphire for the growth of ZnO layers. However, the direct growth of high-quality ZnO on Si was found to be difficult, probably due to the larger value of the formation enthalpy of SiO$_2$ ($\Delta H = 910.7 \pm 1.0$ kJ/mol) compared to that of ZnO ($\Delta H = 350.46 \pm 0.27$ kJ/mol) [7] which makes it easier to form silicon dioxide. In fact, no ZnO growth on Si was found experimentally when N$_2$O was used as an oxidation source.

These problems must be overcome by an appropriate surface treatment technique such as the nitridation of the surface of Si [8] or the deposition of ZnS [9], CaF$_2$ [10] and GaN [11] prior to the ZnO growth. However, the insertion of an insulating layer such as SiN or CaF$_2$ kills the electrical connection between a ZnO layer and a Si substrate. In addition, the diffusion of atoms and the generation of defects caused by the hetero-interface can degrade the qualities of the ZnO layers. On the other hand, direct growth of ZnO/Si was demonstrated using nitrogen oxide (NO$_2$) [12], which was more reactive with DEZn compared to N$_2$O. This strong reactivity was preferable for the bonding of ZnO on Si, nevertheless prereaction in the gas phase could not be ignored and the crystallinity of ZnO grown using NO$_2$ was poor. Therefore, in this study as shown in Fig. 1, we propose the use of a thin ZnO layer grown on Si using NO$_2$ (ZnO/Si) as an underlying layer for the following MOVPE-ZnO growth using N$_2$O. The properties of MOVPE-ZnO on ZnO/Si layers were then investigated.

### 2. Experiments

As mentioned above, DEZn and NO$_2$ were used for the growth of the underlying ZnO/Si, while N$_2$O was used for the subsequent growth of ZnO. Typical flow rates of DEZn and NO$_2$ for the underlying ZnO/Si were $1 \times 10^{-6}$ and $1 \times 10^{-4}$ mol/min, while those of DEZn and N$_2$O for the following ZnO layer on ZnO/Si were $5 \times 10^{-7}$ and $1.25 \times 10^{-2}$ mol/min, respectively. For both growths, electronic grade (6N) N$_2$ gas was used instead of H$_2$ as the carrier gas to avoid etching of the surface of the ZnO layer. Substrate temperature and total pressure of the reactor were kept at 500°C and 6 Torr for the underlying ZnO/Si to suppress prereaction, and at 800°C and 200 Torr for the main ZnO layer. After etching the native oxide from the n-type (001) Si substrates by immersion in HF solution, thermal treatment at 1000°C in the reactor was carried out for the removal of any residual oxide layer. The thickness of the underlying ZnO layer directly grown on the Si was 100 Å and that of the main subsequent ZnO growth was about 2 μm.

Surface morphology was examined using atomic force microscopy (AFM) with a model SPI-3700 (Seiko Instruments) in a constant force mode. PL spectra were taken using excitation with a He–Cd laser (325.0 nm, 10 mW) with the aid of the multichannel CCD system with a maximum resolution of 0.4 meV. CuK$_{\alpha 1}$ (1.5405 Å) was used for the X-ray diffraction measurements.

### 3. Results and discussion

Fig. 2 shows the PL spectra from the underlying ZnO grown directly on Si using NO$_2$. Band edge emission originated from the recombination of the free exciton (EX) emission. Less deep emission was observed at room temperature. This result is quite different from the case of MBE, where no emission could be observed from ZnO grown directly on Si.
suggesting the potential value of MOVPE for ZnO growth. In contrast, however, the broad bound exciton (BX) significant emission PL spectra at 9 K shown in Fig. 2 suggested incorporation of impurities, which probably come from the low-purity (3 N) NO₂, the only available source at present. Also in the X-ray diffraction pattern shown in Fig. 3(a), no diffraction related to ZnO was observed, implying that the size of ZnO grains were small probably like nanocrystalline. At the same time, the surface morphology was poor, i.e., the value of the root mean square (RMS) was 45 nm, which might be caused by prereaction in the gas phase.

The surface of the underlying ZnO layer should be prepared to be flat prior to the growth of the main ZnO layer. Hence, thermal treatment in the reactor under a flow of N₂ was employed aiming at improving the surface roughness and crystallinity as was in the case of MBE-grown ZnO [2,13]. However, the RMS did not change when treated at a flow of 800°C, while it increased to 73 nm using 1000°C. As for the crystallinity, as shown in Fig. 3(b), the appearance of diffraction from ZnO (0 0 0 2) after treatment at 800°C implies that the ZnO layer has crystallized, while no crystallization happened when it was treated at 1000°C probably a result of strong interdiffusion or heavier generation of oxygen vacancies. These results were in contrast to the previous ones where a smooth surface has resulted by the thermal treatment on sapphire [2,13], but it was interpreted to be due to both poor crystallinity of the as-grown ZnO/Si and heavy interdiffusion at the ZnO/Si interface during the treatment.

As mentioned above, the use of NO₂ made it possible to grow ZnO due to its high reactivity, however, the PL qualities of ZnO grown with NO₂ were poor compared with that using N₂O. Therefore, the main ZnO layers were grown using N₂O on the underlying ZnO/Si layers. Successive MOVPE-ZnO growth on ZnO/Si treated at 800°C has revealed it to be remarkably c-axis oriented, as shown in Fig. 3(c). In the PL spectra, as shown in Figs. 4(a) and (b), the underlying ZnO/Si exhibited deep level emissions around 2.4 eV after the treatment. The deep levels are considered to be generated during the thermal treatment. Here, the one treated at 1000°C significantly degrades the optical qualities due to the heavier thermal damage discussed above. The PL spectra of the following 2 μm-thick MOVPE-ZnO grown on those ZnO/Si underlying layers are shown in Figs. 4(c) and (d). The deep emissions appear higher in Fig. (d), whose underlying ZnO was treated at 1000°C, compared with Fig. (c). The intensity of the band edge EX emission is weaker in Fig. (d). This implies that in the growth on Si...
using ZnO/Si as the underlying layer, the ZnO/Si should be treated at 800°C, rather than at 1000°C.

Finally, the PL spectrum of MOVPE-ZnO on ZnO/Si treated at 800°C at 9K is shown in Fig. 5. It was found that the PL intensity of MOVPE-ZnO was 50 times larger than that of the underlying layer. In addition to the 3 meV of FWHM of BX emission, phonon replicas up to the second one of the BX emission were observed. The peak positioned at 3.326 eV labeled as A has not been identified yet, but a similar peak has been observed in high-quality ZnO layers [2,14]. It should be noticed that the EX emission is clearly observed, suggesting less impurity incorporation and good crystallinity as discussed in case of the MOVPE-ZnO on MBE-ZnO/sapphire [2].

The ratio between the peak emission around 2.4 eV and band edge emission was below 10^{-3}, showing that good optical quality was obtained by using the present growth technique. Electrical measurements on In/n-ZnO/n-Si/Al have shown that carriers can be injected from Si, suggesting that any SiO_2 layer, if it exists, at the interface would not have a significant influence on the electrical conduction between ZnO and Si.

4. Conclusions

ZnO layers were grown homoepitaxially on ZnO/Si by MOVPE using DEZn and N_2O. The underlying ZnO grown directly on Si using NO_2 shows dominant band edge emission together with less deep emissions in PL. Thermal treatment did not result in a flat surface, but enhanced the c-axis orientation at 800°C. However, diffusion at the ZnO/Si interface occurred, and it should be minimized. MOVPE-ZnO on ZnO/Si has revealed a c-axis orientation and high optical quality such as 3 meV FWHM for the BX emission and the appearance of EX emission at 9K was observed using the optimum pretreatment condition for the underlying ZnO/Si of 800°C. It is concluded that if appropriate buffer layers on substrates are applied and optimum surface treatment of the buffer layers are conducted, the MOVPE can be a promising technique to grow high quality ZnO on Si.

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References