Structural and optical properties of annealed Ga_2O_3 films on Si(111) substrates

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An investigation has been made into the structural and optical properties of gallium oxide Ga_2O_3 films grown on Si(111) substrates by the metal organic chemical vapour deposition (MOCVD) technique, and annealed in the temperature range 750–1050°C. Post-deposition annealing of amorphous Ga_2O_3 was found to generate β phase grains. Photoluminescence spectra indicated that the annealed Ga_2O_3 films had a blue-green emission at 470 nm and an ultraviolet emission at 365 nm. *BCT/0401*

Keywords: Gallium oxide, Metal organic chemical vapour deposition, Photoluminescence, Post-deposition annealing, Thin films.

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INTRODUCTION

Since metal oxides exist in a variety of compositions and crystal structures and their properties vary widely from insulators to superconductors, applications for metal oxide thin films in advanced technologies are rapidly expanding. Gallium oxide Ga_2O_3 crystals in particular have recently attracted considerable attention as materials for the new generation of optoelectronic devices,[1–5] since they are transparent in a wide range of ultraviolet light down to 280 nm and are potentially electroconductive. These characteristics originate from their band gaps of about 4·8 eV and *n* type semiconductivity. Additionally, Ga_2O_3 has been considered to be one of the most promising materials for use as a metal oxide gas sensor,[6–8] owing to its *n* type semiconductivity and stability in the high temperature range over 600°C.[9]

Although various techniques have been employed to prepare Ga_2O_3 films,[10–18] the metal organic chemical vapour deposition (MOCVD) method offers more flexibility for the growth of metal oxides. This method has the additional advantages of producing uniform, pure, reproducible, adherent and good step coverage films. However, in spite of these advantages, there are only few published reports on growth of Ga_2O_3 thin films by MOCVD techniques, and the precursors of $Ga(hfac)_3$, $Ga[OCH(CF_3)_2]_3{\cdot}HNMe_2$, $[Ga(\mu\text{-O-t-Bu})(O\text{-t-Bu})_2]_2$ and $Ga(O^iPr)_3$ have been investigated.[19–22]

In the present work, Ga_2O_3 thin films were deposited on Si(111) substrates at a temperature of 550°C, using a conventional precursor of trimethylgallium (TMGa). Since Ga_2O_3 is known to transform to its stable β phase above 600°C, the thin films were annealed at temperatures in the range 750–1050°C. The effects of annealing on structural properties were then studied, by comparing the annealed films with as grown films using scanning electron microscopy, X-ray diffraction analysis and atomic force microscopy (AFM). The optical properties of the annealed Ga_2O_3 films were also investigated using room temperature photoluminescence (PL).

EXPERIMENTAL PROCEDURES

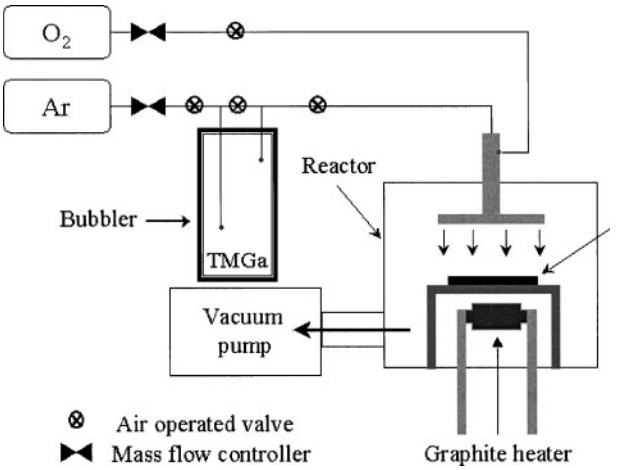
The Ga_2O_3 films were deposited on *p* type Si substrate with (111) orientation, which was cleaned with organic solvents and dried before loading into the system. A schematic diagram of the MOCVD system is shown in Fig. 1. TMGa and O_2 were used as sources. High purity Ar passed through the TMGa bubbler, which was maintained at a temperature of −5°C, and delivered the TMGa vapour to the reactor. The Ga_2O_3 film was synthesised by supplying O_2 and Ar carrier gases at flowrates of 30 smL min^{-1}, and the reaction temperature was set at 550°C. As grown film exhibited a uniform and smooth surface.

After deposition of the Ga_2O_3 film, samples were annealed in a quartz tube furnace at temperatures in the range 700–1050°C for 1 h in ambient air. The structural characteristics of the films were analysed by SEM (Hitachi S-4200) and XRD (Philips CM20T, 200 kV) with Cu $K_{\alpha 1}$ radiation (λ=0·154056 nm). Surface roughness was measured using AFM (Nanoscope III, Digital Instruments) with a scan size of 10×10 μm. PL measurements were carried out at room temperature with a Shimadzu fluorescence spectrophotometer (RF-5301PC). The excitation light was the monochromatic light from a xenon short arc lamp with a wavelength of λ=250 nm.

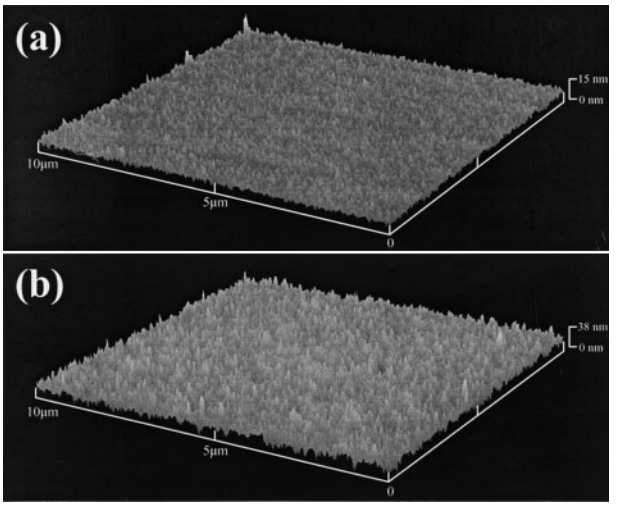
RESULTS AND DISCUSSION

Figure 2 shows SEM images of as grown, 900°C annealed and 1050°C annealed Ga_2O_3 thin films. Plain view SEM images indicate that microstructure is transformed by the thermal annealing process to grainlike structures. Furthermore, the size of the grainlike structures grows with increasing annealing temperature in the range 900–1050°C. Cross-sectional SEM images also indicate that although no clear grain boundaries are found inside as grown Ga_2O_3 thin films, grainlike structures appear following annealing. Statistical analysis of many cross-sectional SEM images shows that both as deposited and annealed films have thicknesses in the range 250 to 300 nm.

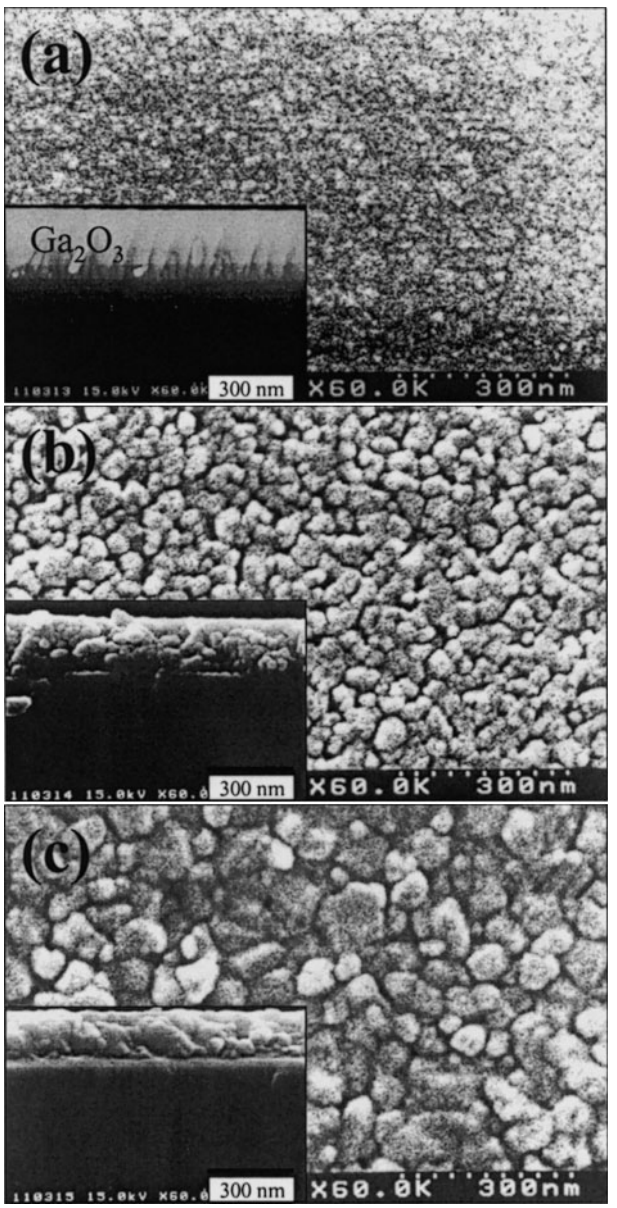
In order to investigate the surface roughness of Ga_2O_3 films grown on Si(111) substrates, AFM analysis was performed. Figure 3 shows AFM topographies representing the surface morphology of as grown and 1050°C annealed Ga_2O_3 films, indicating that the size of the grainlike structure on top of the Ga_2O_3 film increases with thermal annealing. The rms surface roughnesses of as grown and 1050°C annealed Ga_2O_3 films were 1·089 and 4·013 nm, indicating that the surfaces of annealed Ga_2O_3 films are rougher than those of as grown films. It is surmised that the surface becomes rougher as a result of the



1 Schematic illustration of MOCVD reactor



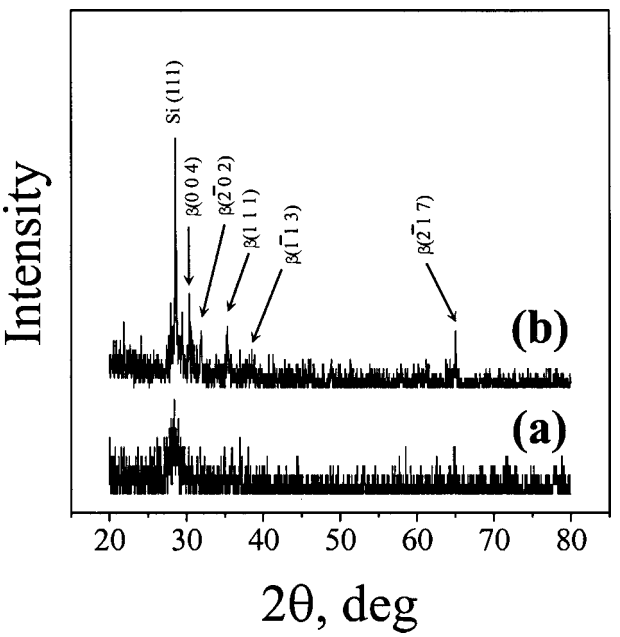
3 AFM images of *a* as grown and *b* 1050°C annealed Ga_2O_3 thin films



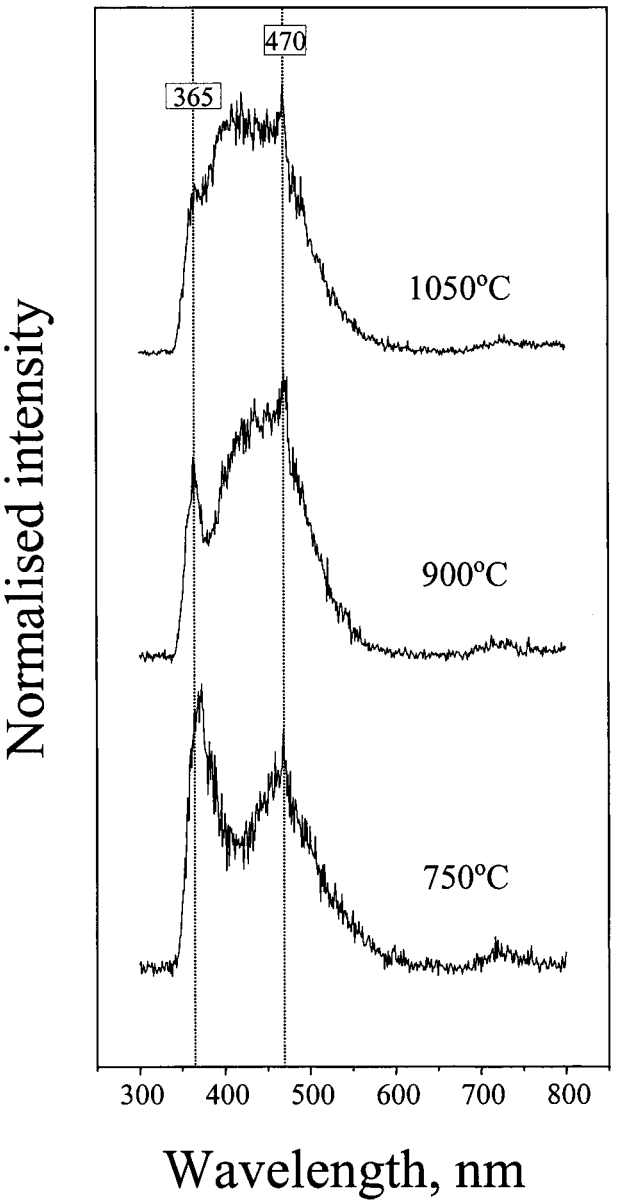
2 Plain view SEM images (with inset cross-sectional SEM images) of *a* as grown, *b* 900°C annealed, *c* 1050°C annealed Ga_2O_3 thin films

appearance of grains on top of the films, and thus the AFM images agree with the SEM images.

In order to investigate the effects of thermal annealing on the crystallinity of Ga_2O_3 thin films, XRD analysis was performed on as grown and 1050°C annealed samples. Figure 4*a* shows the XRD diffraction pattern of an as grown film. Owing to the absence of a distinguishable Ga_2O_3 diffraction peak, it is supposed that the Ga_2O_3 films have an amorphous structure. Figure 4*b* shows the diffraction pattern of the 1050°C annealed Ga_2O_3 film: the lines observed in this diffractogram are found to coincide with the (004), ($\bar{2}$02), (111), ($\bar{1}$13) and ($\bar{2}$17) peaks of β-Ga_2O_3 obtained from JCPDS card 43–1012. The stable β-Ga_2O_3 phase is known to have monoclinic structure.[23] The existence of the β-Ga_2O_3 peaks indicates the production of β-Ga_2O_3 grains on Si(111) substrates by thermal annealing at sufficiently high temperature. The present experiments showed that the crystalline orientation of the Ga_2O_3 thin film was not significantly influenced by the orientation of the Si substrate (not shown here).



4 XRD patterns of *a* as grown and *b* 1050°C annealed Ga_2O_3 thin films



5 Room temperature PL spectra of Ga_2O_3 films annealed at temperatures in range 750–1050°C

Figure 5 shows PL spectra of Ga_2O_3 films annealed in the range 750–1050°C, recorded at room temperature (27°C). The dominant emissions from all three films are bands located at wavelengths of around 470 nm (2·645 eV) and 365 nm (3·405 eV), respectively in the blue-green and ultraviolet spectral regions. UV luminescence of Ga_2O_3 has been reported to be attributable to an intrinsic transition due to the recombination of a self-trapped exciton.[24]

It is noteworthy that a strong and broad emission in the blue light range appears with thermal annealing at a higher temperature of 1050°C. Since annealing in a reducing atmosphere favours the formation of oxygen vacancies and blue emission is enhanced,[25,26] it is surmised that the use of ambient air in annealing experiments at a high temperature of 1050°C favours oxygen vacancies, contributing to the appearance of blue emission. Further systematic study is necessary to reveal the mechanism of the observed emissions.

CONCLUSIONS

Gallium oxide Ga_2O_3 films have been prepared on Si(111) substrates by reacting a TMGa and O_2 mixture and the effects of post-deposition annealing have been investigated. SEM images indicate that grainlike structures appear following thermal annealing, and AFM imaging reveals that the rms surface roughness is increased by thermal annealing. The XRD data indicate that even though as grown Ga_2O_3 films turn out to be amorphous, β-Ga_2O_3 phase appears on annealing. Photoluminescence spectra of annealed Ga_2O_3 films reveal dominant emission in the BG and UV regions. Annealing at 1050°C helps the Ga_2O_3 films to emit blue light.

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