Determination of the mechanical properties of r.f.-magnetron-sputtered zinc oxide thin films on substrates

Min-Yung Han, Jwo-Huei Jou

Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30043, Taiwan

Received 29 July 1994; accepted 15 November 1994

Abstract

The variation of stress with respect to temperature in ZnO films, prepared by r.f. magnetron sputtering on Si and GaAs substrates, has been studied by using a bending beam technique. The thermal expansion coefficients and biaxial moduli of the films have been determined from the stress–temperature curves upon cooling. For most of the films, the obtained biaxial modulus ranges from 250 to 360 GPa at temperatures from 25 to 400 °C, whilst the thermal expansion coefficient increases from $5 \times 10^{-6}$ to $8 \times 10^{-6} \, \text{°C}^{-1}$. X-ray diffraction results reveal that the films deposited at a higher total gas pressure, i.e. 5.3 Pa, or a lower substrate temperature, i.e. 250 °C, have further crystallized upon annealing. The crystallization has caused the films to exhibit an irreversible stress behaviour upon thermal cycling.

Keywords: Deposition process; Elastic properties; Stress; Zinc oxide

1. Introduction

Measurement of the mechanical properties of thin films is known to be difficult. Some measurements have been performed on free-standing thin films [1–3]. The biaxial moduli of free-standing thin films may be different from those of the films adhering to a substrate. Besides, only the tensile or non-stressed biaxial moduli of the thin films can be obtained from the free-standing situation. Other papers have, however, revealed that the biaxial moduli of thin films, in tensile or compressive stress state, can be determined from the measurement of thermal stress by depositing the films on two different substrates [4–6]. The biaxial moduli and thermal expansion coefficients of thin films can be obtained from the stress–temperature curves through the following equations [5, 6]:

$$
\sigma_{i, 1} = \frac{1}{6} \frac{E_i}{1 - \nu_i} \frac{d_i^3}{d_i} \left( \frac{1}{R_i} - \frac{1}{R_0} \right)
$$

$$
\frac{\text{d} \sigma_{i, 1}}{\text{d} T} = \frac{E_i}{1 - \nu_i} (\alpha_i - \alpha_t)
$$

$$
\frac{\text{d} \sigma_{i, 2}}{\text{d} T} = \frac{E_i}{1 - \nu_i} (\alpha_2 - \alpha_t)
$$

$$
\frac{E_i}{1 - \nu_i} = \frac{\text{d} \sigma_{i, 2}}{\text{d} T} - \frac{\text{d} \sigma_{i, 1}}{\text{d} T}
$$

$$
\alpha_t = \frac{C \alpha_2 - \alpha_1}{C - 1}
$$

where

$$
C = \frac{\text{d} \sigma_{i, 1}}{\text{d} T} \frac{\text{d} \sigma_{i, 2}}{\text{d} T}
$$

$\sigma_{i, 1}$ ($i = 1, 2$) is the thermal stress in the film coated on the $i$th substrate. $E_i/(1 - \nu_i)$ is the biaxial modulus of the $i$th substrate. $d_i$ is the thickness of the $i$th substrate. $d_t$ is the thickness of the film. $1/R_i$ and $1/R$ are the curvatures of the substrates before and after the deposition of the film. $E_i/(1 - \nu_i)$ is the biaxial modulus of the film. $\alpha_i$ and $\alpha_t$ are the thermal expansion coefficients of the $i$th substrate and the film respectively.

The biaxial moduli determined using the above method may be more authentic to reflect the mechanical characteristics of the desired thin films that deposit on substrates. In addition, thermal expansion coefficients of the thin films can be obtained at the same time. Hence the latter method is employed to determine the mechanical properties of ZnO thin films in this study. The effect of processing conditions on the properties has been examined.
Table 1

Thermal expansion coefficients $\gamma_{Si}$ and $\gamma_{GaAs}$ and biaxial moduli $E_{Si}/(1 - \nu_{Si})$ and $E_{GaAs}/(1 - \nu_{GaAs})$ of the Si and GaAs substrates used at temperatures ranging from 30 to 400 °C

<table>
<thead>
<tr>
<th>Property$^a$</th>
<th>Temperature dependence$^b$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{Si}/(1 - \nu_{Si})$</td>
<td>$176.4 - 5.46 \times 10^{-7}T - 2.46 \times 10^{-5}T^2$</td>
<td>[9]</td>
</tr>
<tr>
<td>+ $1.72 \times 10^{-8}T^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{GaAs}/(1 - \nu_{GaAs})$</td>
<td>$123.3 - 1.42 \times 10^{-7}T - 3.18 \times 10^{-6}T^2$</td>
<td>[10]</td>
</tr>
<tr>
<td>+ $3.73 \times 10^{-9}T^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_{Si}$</td>
<td>$2.38 + 7.49 \times 10^{-12}T - 1.28 \times 10^{-5}T^2$</td>
<td>[11]</td>
</tr>
<tr>
<td>+ $8.77 \times 10^{-9}T^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_{GaAs}$</td>
<td>$5.34 + 9.66 \times 10^{-12}T - 2.33 \times 10^{-5}T^2$</td>
<td>[12]</td>
</tr>
<tr>
<td>+ $7.17 \times 10^{-9}T^3$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$The unit of $E/(1 - \nu)$ is gigapascals (or $10^9$ N m$^{-2}$) and that of $\alpha$ is $10^{-6}$ C$^{-1}$ (or ppm C$^{-1}$).

$^b$T is in kelvins.

2. Experiment

The ZnO films studied were prepared by r.f. magnetron sputtering on 3 in (100) orientation Si and GaAs substrates. The thicknesses of the substrates, i.e. $d$, are 380 ± 1 µm for the Si substrate and 520 ± 2 µm for the GaAs substrate. The thicknesses of the films were measured by using an x step profilometer with a resolution of 500 Å. The sputtering chamber was evacuated to less than $6 \times 10^{-6}$ Torr before sputtering. Various processing parameters were examined to understand their effects on the stress behaviour and mechanical properties of the films. They are total gas pressure, substrate temperature, pressure ratio of Ar to O$_2$, and sputtering power.

Thermal stresses in these ZnO films were determined by using a bending-beam apparatus while thermally cycling the specimens from 25 to 400 °C. Experimental details of this bending-beam stress measurement can be referred to in Refs. [7] and [8]. The material constants of the substrates used in the calculations of the biaxial modulus and thermal expansion coefficient of the films are tabulated in Table 1. These material constants are given as a function of temperature since they are temperature dependent. The magnitudes of $E_{Si}/(1 - \nu_{Si})$, $E_{GaAs}/(1 - \nu_{GaAs})$, $\alpha_{Si}$ and $\alpha_{GaAs}$, are respectively taken from Ref. [9], Ref. [10], Ref. [11] and Ref. [12].

The bending-beam apparatus has a resolution of 0.03 m$^{-1}$ in measuring the absolute curvature of the specimen and 0.002 m$^{-1}$ in measuring the curvature variation during thermal cycling. Three to five specimens are prepared for each processing condition. A reasonably good sample-to-sample reproducibility is obtained in each thermal stress measurement except for the films deposited at a total gas pressure of 5.3 Pa. The error percentage obtained in the calculation of the biaxial moduli is ± 19% for the ZnO films deposited at 5.3 Pa and ± 12% for those deposited under the other conditions. The error percentage of the calculated thermal expansion coefficients is ± 4% for the ZnO films deposited at 5.3 Pa and ± 2% for those deposited under the other conditions.
3. Results and discussion

3.1. Effect of total gas pressure

Fig. 1 shows the variation of stress in the films of ZnO deposited on Si and GaAs substrates as a function of the temperature. The thicknesses of the films range from 1.1 to 1.3 μm. The sputtering conditions for the films were set at a total gas pressure of 0.5 Pa, power 200 W, Ar-to-O₂ pressure ratio 1:1, and substrate temperature 350 °C. The stress curves upon heating and cooling fall on each other for the film on the Si substrate, and this is also true for that on GaAs. This reversible stress behaviour indicates no structural change or stress relaxation occurring in the films during thermal cycling. Therefore the variation of the stress can be said to result solely from the thermal mismatch between the films and substrates. The thermal mismatch has contributions from the different thermal expansion coefficients of the films and substrates. The stress–temperature curves have different slopes for the films on the two different substrates. This is mainly because the thermal mismatches are different for the films on the...
two different substrates. The residual stress at room temperature is less compressive in the films on GaAs than that on Si. This is because the ZnO films grown on GaAs are less crystalline than those on Si. A less marked peening effect is therefore expected to occur on the films grown on GaAs [13].

Similar reversible stress behaviour has been observed for the films deposited at a higher total gas pressure of 1.1 Pa, as shown in Fig. 2. The residual stress of the films at room temperature is, however, notably different from that of the aforementioned films. This may be attributed to a less marked peening effect as the total gas pressure increases [14, 15].

The films exhibit different stress behaviours when the total gas pressure further increases to 2.1 Pa, as shown in Fig. 3. That is that the stress curves no longer fall on each other during heating and cooling. Especially for the films on Si, a very marked irreversible stress behaviour can be observed. The irreversible stress behaviour is not obvious for the films on GaAs. Such a behaviour is more marked for the films on either sub-

strate as the total gas pressure further increases to 5.3 Pa, as shown in Fig. 4. These irreversible phenomena may be due to recovery and/or grain growth of the films. This can actually be demonstrated by the X-ray
diffraction results for the films. As shown in Fig. 5, for the films deposited at 5.3 Pa on both substrates, the diffraction intensities of the films are higher after annealing than as deposited. The films must have further crystallized upon thermal cycling. This reveals why the stress behaviour is not reversible during thermal cycling.

Generally speaking, the density of a given material will increase during crystallization, which will in turn result in a tensile stress in the film. Crystallization-induced tensile stress is a frequently observed phenomenon in thin films that deposit on substrates. For bulk materials, annealing may result in stress relaxation, whilst for thin films on substrates annealing would very frequently result in a stress increment toward the higher tensile or lower compressive stress state. In this study, the compressive residual stress in the films has been observed to decrease upon annealing. The decrease in the compressive stress may be solely attributed to the crystallization effect, or it may also be partly attributed to the effect of stress relaxation [16]. However, further investigation is needed to confirm the latter postulation.

To calculate correctly the thermal expansion coefficient and the biaxial modulus of the film, the stress curves upon cooling are used to determine the slope, $\frac{\Delta \sigma}{\Delta T}$ according to Eqs. (3) and (4). This is because no structural change is believed to occur further upon
cooling after the film has been annealed to the elevated temperature. The stress variation occurring upon cooling should be purely due to the thermal mismatch between the film and substrate. Fig. 6(a) shows the thermal expansion coefficients of the ZnO films deposited at different total gas pressures. The thermal expansion coefficients of the ZnO films deposited at the total gas pressure of 5.3 Pa, are obviously smaller than those of films deposited at 0.5, 1.1 and 2.1 Pa. The ZnO films deposited at 5.3 Pa are presumed to have a structure different from those deposited at the other gas pressures despite the fact that they show a sample-to-sample reproducibility poorer than the others. However, more investigations are needed to prove this postulation. For all the other ZnO films, the calculated thermal expansion coefficient increases from $5 \times 10^{-6}$ to $8 \times 10^{-6} \, \text{C}^{-1}$ at temperatures increasing from 25 to 400 °C. The calculated biaxial moduli are shown in Fig. 6(b). No systematic variation can be observed when the total gas pressure changes from 0.5 to 5.3 Pa. They vary slightly from one another within the experimental uncertainty. Their magnitudes vary from 280 to 360 GPa at observation temperatures from 25 to 400 °C.

3.2. Effect of substrate temperature

As shown in Fig. 7, a reversible thermal stress behaviour was also found when the substrate temperature was increased to 450 °C while the other parameters were kept the same, i.e. total gas pressure 0.5 Pa, power 200 W and Ar-to-O$_2$ pressure ratio 1:1. However, an irreversible thermal stress behaviour, as shown in Fig. 8, was found when the substrate temperature was decreased to 250 °C. The irreversible thermal stress behaviour may also be attributed to the crystallization of the ZnO films mentioned previously. This can be demonstrated by the increase of intensity of their X-ray diffraction peaks upon annealing.

Figs. 9(a) and 9(b) show the thermal expansion coefficients and biaxial moduli of the ZnO films deposited at different substrate temperatures. Similarly, they are not much affected by the substrate temperature within the studied range. The only exception is the biaxial modulus of the film deposited at 450 °C, i.e. it is slightly smaller than those of the other films throughout the entire range of observation temperatures.

3.3 Effect of Ar-to-O$_2$ pressure ratio

Reversible thermal stress behaviour is also observed in the films of ZnO deposited on Si and GaAs substrates at various Ar-to-O$_2$ pressure ratios. In these experiments, the total gas pressure was set at 0.5 Pa, power at 200 W, and substrate temperature at 350 °C. Fig. 10 shows the variation of thermal stress during cooling of the ZnO films sputtered at various Ar-to-O$_2$ pressure ratios. The thermal stress curves have very similar slopes for the different ZnO films on Si. This is also true for those on GaAs. The similar slopes indicate that the ZnO films deposited at the different Ar-to-O$_2$ pressure ratios have similar mechanical properties, i.e. thermal expansion coefficient and biaxial modulus.

The thermal expansion coefficients and biaxial moduli of the ZnO films deposited at the different Ar-to-O$_2$ pressure ratios are shown in Figs. 11(a) and 11(b). However, no significant or systematic variation can be observed when the pressure ratio of Ar to O$_2$ is changed from 0.33 to 3. The only exception is the biaxial modulus of the films deposited at the 1:1 pressure ratio of Ar to O$_2$, i.e. it is slightly larger than those of the other films throughout the entire range of observation temperatures. It varies from 340 to 350 GPa at temperatures from 25 to 400 °C, while the films deposited under the other two sets of conditions have biaxial moduli varying from 260 to 330 GPa. It is difficult at the moment to conclude whether the above difference is real or not since the difference is not significantly large enough to distinguish from the experimental uncertainty, i.e. ±2% for these measurements.

3.4. Effect of sputtering power

Similar reversible thermal stress behaviour is observed for the ZnO films deposited on Si and GaAs at sputtering power varying from 100 to 300 W. In these experiments, the total gas pressure was set at 0.5 Pa, the Ar-to-O$_2$ pressure ratio at 1:1, and the substrate temperature at 350 °C. Fig. 12 shows the variation of thermal stress during cooling in the ZnO films sputtered at the different sputtering powers. The stress curves have very similar slopes for the ZnO films sputtered at different sputtering powers. Again, the mechanical properties of the ZnO films are shown not to vary much with variations in the sputtering power from 100 to 300 W.

The thermal expansion coefficients and biaxial moduli of the ZnO films are shown in Figs. 13(a) and 13(b). No significant or systematic variation can be observed when the sputtering power is changed from 100 to 300 W. The only exception is the calculated biaxial modulus of the films deposited at a sputtering power of 200 W. It is slightly larger than those of the other films throughout the entire range of observation temperatures; i.e. it is at most 20% greater than the others. The difference is, however, not marked enough to distinguish from the experimental uncertainty scale, i.e. 24% or ±12%. It may be true that the mechanical properties of the ZnO films are not sensitive to the variation of the parameters within the studied ranges. This may explain why they show little significant variation in the obtained mechanical properties with respect to varying processing parameters.
Due to the limitations of the processing, the studied parameters cannot, however, be varied easily over a wider range. For later studies, it is suggested that more specimens of the same batch be prepared for the measurements so that better sample statistics can be obtained and the experimental uncertainty can be reduced. The dependence of the mechanical properties on the processing parameters can hopefully be better understood.

4. Summarizing remarks

The thermal expansion coefficients and biaxial moduli of the sputtered ZnO films were obtained from the measurement of thermal stress of the films on Si and GaAs substrates. With a few exceptions, they do not vary significantly with the variation of total gas pressure from 0.53 to 2.1 Pa, substrate temperature from 250 to 450 °C, Ar-to-O₂ pressure ratio from 0.3 to 3, and power from 100 to 300 W. For most of the films, the obtained biaxial modulus ranges from 250 to 360 GPa at temperatures from 25 to 400 °C, whilst the thermal expansion coefficient increases from 5 × 10⁻⁶ to 8 × 10⁻⁶ °C. The X-ray diffraction results reveal that the films deposited at a higher total gas pressure, i.e. 5.3 Pa, or lower substrate temperature, i.e. 250 °C, have further crystallized upon annealing. This causes the films to exhibit an irreversible stress behaviour.

Acknowledgments

The authors would like to thank Dr. Li Hsu (currently with Choung-Shan Institute of Science and Technology) and Dr. Duen-Jen Cheng (Materials Research Laboratories, Industrial Technology Research Institute) for their help in preparing the films studied. Financial support in part from the National Science Council, Taiwan, through Projects NSC-82-0405-E-007-253 and NSC-83-0405-E-007-045, and Tsing-Hua University through the Academic Research Funding Program is gratefully acknowledged.

References