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Nanocrystalline zirconium oxide thin films grown under low pulsed dc voltages

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Abstract
Zirconium oxide thin films were deposited at room temperature by an off-plane filtered cathodic vacuum arc under a pulsed substrate bias between 0 and \(-250\) V. The film properties including structure, surface morphology, mechanical and optical properties on n-Si(1 0 0) and quartz were investigated in terms of substrate bias. The results show that a strong effect of substrate bias on the film properties on n-Si(1 0 0) has been observed. With increasing substrate bias, the film changes from an amorphous state at floating bias to a randomly oriented crystalline structure at \(-100\) V, and then to a preferred orientation along the [2 0 0] direction at \(-250\) V. The stoichiometric ratio is decreased with increasing substrate bias as well as deposition rate. The film surface remains smooth at floating bias while large roughness is found when biases were applied. Besides, it is also observed that both hardness and Young’s modulus increase with the substrate bias. However, for the films on quartz substrate, nanocrystalline film was found only at \(-250\) V. Optical properties including optical constants and optical band gap (\(E_g\)) were investigated. The mechanisms of changes in structure and related properties were discussed.

1. Introduction

Recently, nanocrystalline ceramics have attracted considerable scientific interest due to their improved properties resulting from grain-size refinement in the nanometre scale. Nanocrystalline zirconium oxide thin films have found applications in many important fields of interest such as thermal barrier coatings, laser coatings, thin film optics, hard overcoats, low thermal conductivity, high refractive index and chemical durability [1, 2].

Many techniques have been used to synthesize zirconium oxide thin films, such as chemical vapour deposition [3, 4], sol–gel techniques [5], ion-beam assisted deposition [6] and sputtering [7–10]. Filtered cathodic vacuum arc (FCVA) as a promising technique has been widely used to deposit metal oxide thin films due to its high ionization rate, high deposition rate and flexibility of target arrangements [11]. Moreover, this deposition technique can provide high ion energy (50–150 eV) to decrease the void volume of the film by increasing the packing density of the microstructure and thus result in a dense film [11]. The intrinsic high ion energy can thus easily contribute to crystal formation at lower temperatures [12].

In our previous work, zirconium oxide thin films by FCVA had been studied under various working pressures and growth temperatures [12, 13], in which nanocrystalline zirconium oxide thin films could be attained under proper growth conditions. It is known that energetic particle bombardment of the film induced by the substrate bias during the film growth has a strong effect on the physical and chemical nature of the resulting films [1]. In this work, by using the FCVA technique, nanocrystalline zirconium oxide thin films were obtained when a lower pulsed dc bias was applied to the substrates at room temperature. Thus, the aim of the work is to investigate the influence of lower dc bias on the properties of the zirconium oxide thin films, and the mechanisms on the variation of film properties are also discussed.

2. Experimental details
Zirconium oxide thin films were deposited by an off-plane FCVA system as described in detail elsewhere [14, 15]. A Zr
cathode with a purity of 99.98% operated at an arc current of 120 A was used to obtain the plasma. The base pressure of the system was around 10⁻⁶ Torr. The MAGPULS power supply generated dc pulsed signal of 20% duty with a frequency of 33 kHz was applied between the substrate holder and the grounded vacuum chamber. The films were grown on n-Si (1 0 0) and quartz substrates without external heating under various bias \( V_b \) (0, −100 and −250 V) while the working pressure was kept at 4.0 × 10⁻³ Torr.

The phase and crystal structure of the zirconium oxide thin films were identified by x-ray diffraction (XRD) with a Cu Kα source. The core level spectra and compositional analysis were performed by x-ray photoelectron spectroscopy (XPS). The surface morphology was performed by AFM in tapping mode (Dimension 3000 scanning probe microscope from Digital Instrument). The hardness and Young’s modulus of the films on silicon versus substrate bias are displayed in figure 3. Both of them increase with the substrate bias. Under floating condition

Figure 1. XRD patterns of zirconium oxide thin films deposited at different substrate bias on silicon and quartz substrates.

Figure 1 shows the XRD patterns for the zirconium oxide thin films deposited under \( V_b = 0 \) V, −100 V and −250 V on silicon and quartz, respectively. Obviously, the evolution of the film structure on silicon significantly differs from that on quartz. Without the substrate bias, the film is amorphous as described by a broad peak centred at 2\( \theta \) = 31.1°. At \( V_b = −100 \) V, significant changes in the film structure are observed, where the film structure has transformed to a polycrystal with the strongest peak at 2\( \theta \) = 27.5° arising from the monoclinic (−1 1 1) (labelled as m(−1 1 1)) plane. With the exception of the weak peak at 2\( \theta \) = 30° from the tetragonal ZrO₂ (1 1 1), the remaining relatively weak peaks are also ascribed to the diffractions from the monoclinic phase. However, the intensity from this tetragonal phase is very weak, implying a small amount of tetragonal ZrO₂ in the film dominated by the monoclinic phase. As the bias continues to increase to −250 V, the peak of the m(−1 1 1) planes obviously becomes weak, accompanied by a decrease in other weak peaks including the t(1 1 1). At the same time, the peaks of m(200) and m(1 2 2) become strong with the strongest one from m(200) instead of m(−1 1 1) at \( V_b = −100 \) V. The variation in XRD patterns with \( V_b \) implies that the preferred orientation of the crystallites in the films occurs along the [2 0 0] direction, while at \( V_b = −100 \) V, the film is polycrystalline without an obvious preferred orientation. Furthermore, full width at half maximum (FWHM) intensity obviously becomes wider corresponding to the finer grain size, which is less than 7 nm decreased from around 11 nm at \( V_b = −100 \) V estimated by the Scherrer equation [16].

Interestingly, the behaviour of structure variation with substrate bias on quartz is not the same as that on silicon, though under the same growth conditions. It could be seen in the figures of \( V_b = 0 \) and −100 V that the amorphous structure still dominates in the film although rather weak peaks from m(−1 1 1), (−2 2 1) and (1 2 2) are observed, denoting a small amount of crystallites in the film at \( V_b = −100 \) V. As \( V_b \) goes up to −250 V, the film crystallizes in the monoclinic phase with the strongest peak arising from the (1 1 1) planes, accompanied by other peaks with various weak intensities also arising from the monoclinic phase. No preferred orientation of the crystallites could be observed, nor tetragonal phase, being different from the results on silicon discussed above. Using the Scherrer equation, the average grain size is less than 15 nm and still in the nanometric scale.

The surface morphology of the films on silicon was performed by AFM. Figure 2 shows the AFM images for the films grown on silicon under various biases. The unbiased film exhibits a very smooth surface as shown in figure 2(a). However, the film roughness dramatically increases as revealed by the vertical scale from 2 nm at \( V_b = 0 \) V to 140 nm at \( V_b = −100 \) V over an area of 1 × 1 \( \mu \)m². Besides, smaller evenly spread particles are clearly observed on the film surface with some much larger particles (around 0.15 \( \mu \)m in size) randomly distributed as shown in figure 2(b). At \( V_b = −250 \) V, these random large particles disappear. Meanwhile, uniformly distributed nanoparticles are obviously observed on the film surface with the size of several tens of nanometres. It is noted that the surface roughness has reduced as the vertical scale decreases to 30 nm, being still higher than that of the film without bias.

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3. Results

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without bias, the measured hardness of 13.5 GPa and Young’s modulus of 197 GPa are completely comparable to the bulk monoclinic ZrO₂, which has a hardness of 10–12 GPa and a Young’s modulus of 168.7 GPa [17]. At \( V_b = -100 \) V, both hardness and Young’s modulus increase compared with the unbiased films. It is interesting to note that the film hardness could achieve nearly 19 GPa at \( V_b = -250 \) V and for Young’s modulus, it is as high as 210 GPa.

The optical properties are investigated for the films on quartz substrates. The optical constants of the films at 550 nm versus \( V_b \) are illustrated in figure 4(a). The increase in the refractive index against \( V_b \) indicates the packing density becomes higher upon the negative bias supplied to the substrate since the refractive index is an indicator of the packing density and it is proportional to the packing density. Meanwhile, the extinction coefficient shows a decreasing trend with increasing \( V_b \). The variation of optical band-gap energy, \( E_g \), determined from the Tauc plot [18], with \( V_b \) is shown in figure 4(b). It is found that \( E_g \) has a tendency towards a low value. It starts from 5.0 eV of the film without bias to 4.85 eV at \( V_b = -100 \) V. As the bias increases to \(-250\) V, \( E_g \) further decreases to 4.75 eV.

4. Discussion

During the film deposition using the ion-beam assisted technique, the ion energy and the ion-to-atom flux ratio are the two important factors that affect the film structure and the resulting film properties [6]. For the FCVA technique, the
plasma expanding from the cathode spots contains ions that are usually multiply charged and have an ion energy, for Zr ions, as high as 112 eV [19]. The ions generated from the vacuum arc plasma will pass through the magnetic filter whereas the neutral atoms will be trapped by the filter and could be considered negligible. It is proposed by Bubenzer et al that ion energy is closely related to the bias voltage and the process pressure by the following expression [20]:

$$E = K V_b/P^m, \quad 0 \leq m \leq 1,$$

where $K$ is a constant, $V_b$ is the bias voltage, $P$ is the process pressure and $m$ is a coefficient. According to this expression, the substrate bias and the process pressure are the important parameters affecting the ion energy.

It is well known that during the film growth by the deposition of energetic ions different mechanisms exist depending on the ion energy [21, 22]. If the ion energy is below the threshold energy for physical sputtering, the film will grow based on subplantation (very shallow implantation) mechanism. When energetic particles interact with a solid surface, the primary particles lose energy by a series of elastic and inelastic collisions with the target atoms. In a subplantation model [23], the energetic atoms participating in the collision cascade dissipate their excess energy to the lattice in a thermalization stage, which results in an increase in the thermal energy of the lattice atoms, and therefore the enhancement of adatom mobility. However, if the ion energy exceeds the threshold energy for physical sputtering, ejection/resputtering occurs during the film growth. In our case, zirconium oxide thin films were grown under the substrate bias of $0 \text{V}, -100 \text{V}$ and $-250 \text{V}$, respectively. According to the equation of ion energy above, the ion energy is proportional to the substrate bias since only bias is changed during the film growth. From our experimental results, different film properties are observed under different bias conditions. These properties suggest that different bias dependent growth mechanisms are involved.

For the films on silicon, under floating condition ($V_b = 0 \text{V}$), the amorphous phase formed in the zirconium oxide thin films may be due to lower atom mobility. At $V_b = -100 \text{V}$, the ion energy is increased resulting in increased adatom surface mobility and enhanced adatom diffusion assuming that subplantation occurs as in [23]. Significant ion energy could be transferred to the atoms on the film surface and the defects in the films annealed out. As a result, free adatoms gather to form randomly oriented crystallites and result in a considerable increase in the surface roughness as larger particles are observed [24] (see figure 2(b)). On further increasing the substrate bias to $-250 \text{V}$, the ion energy obtained is quite high and the mobility of the atoms on the growing film surface is considerably increased. However, it is found that the deposition rate decreases from $43 \text{ nm min}^{-1}$ at $V_b = -100 \text{V}$ to $38 \text{ nm min}^{-1}$ at $V_b = -250 \text{V}$. At $V_b = -250 \text{V}$, the decrease in the deposition rate implies breaking of atomic bonds and ejection/resputtering of the adatoms occur during the film growth. By the same FCVA deposition technique, it was reported that resputtering occurred in a similar substrate bias range (more negative than $200 \text{V}$) for other thin films, such as copper and (Ti, Al)N [24, 25]. Besides, the decrease in the stoichiometric ratio from 2.1 to 1.95 observed by XPS measurements at this high substrate bias is possibly due to high energy induced lattice defects, such as oxygen vacancies. Similar results were also reported in the literature [1], where the stoichiometric ratio of O/Zr decreases from 2.02 to 1.89 as the substrate bias increases from 0 to $-50 \text{V}$. Moreover, if the energy of the displaced atom is greater than the threshold energy, it triggers secondary collisions and more collisions, which lead to the formation of a highly distorted atomic network. In this case, equilibrium large crystallites are hard to form, which results in a decrease in the crystalline size in the films deposited at a high substrate bias corresponding to the broadening of XRD lines at $V_b = -250 \text{V}$. In addition, the result of energetic bombardment during deposition is that topographical features that protrude up from the rest of the surface plane are more rapidly sputtered than the flat surfaces. Thus the result of self-sputtering is the decrease in the surface roughness as shown in figure 2(c) [24]. Meanwhile, at $V_b = -250 \text{V}$, the film structure has a preferred orientation along [2 0 0]. It is known that different crystallographic orientations have different sputter yields [26]. In a polycrystalline film, grain orientations with higher sputter yields are removed faster by sputtering. The newly deposited layer grows epitaxially on the grains with low sputter yield orientation, and these grains will eventually dominate the film. The plane along the [2 0 0] direction has a lower sputter yield as it shows the more open channeling direction in the monoclinic structure of ZrO$_2$, and thus lower lattice damage. Therefore, the formation of the [2 0 0] preferential orientation of the films deposited at $-250 \text{V}$ is attributed to the sputter channeling effect.

The variation of film hardness and Young’s modulus with $V_b$ is closely associated with the microstructure of the film. It is found that the film hardness is increased at $V_b = -100 \text{V}$ compared with the amorphous film at $V_b = 0 \text{V}$. Cheng et al also observed the increased hardness when a (Ti, Al)N film

![Figure 4. Optical constants at 550 nm and $E_g$ as a function of oxygen flow rate.](image-url)
changed from the amorphous state to the crystalline state [24]. Meanwhile, it is noted that considerable increase in hardness occurs from 14.4 GPa at $V_b = -100$ V to 19 GPa at $V_b = -250$ V. It should be recalled that in the previous XRD study the corresponding average grain size in the films reduces from 11 to 7 nm, which contributes to the increment of hardness and Young’s modulus induced by the Hall–Petch effect [27].

However, the observed behaviour of the film structure on the quartz substrate differs from that on n-Si(100), although under the same growth condition. Similar behaviour was found in the work of Wong et al [28], where a strong effect was found on the crystallinity of zirconium oxide thin films on conducting substrates, but it had less effect on insulating substrates. The difference is believed to be due to the electrical characteristics of the substrate materials [28]. It is known that n-Si(100) is electrochemically active, while quartz is a non-conductor. When the substrates are coated with zirconium oxide thin film, they become a capacitor in the bias sputtering circuit. The substrate bias affects the film structure only when the total thickness of the insulating layer is sufficiently small [28]. In our case, the total thickness including quartz and the thin films is large and thus the substrate bias is not so effective. In addition, on increasing substrate bias, the knock-on atoms may penetrate deeper into the film on quartz where they become trapped as interstitials, thus resulting in a densely packed structure. This corresponds to the increase in the refractive index. On the other hand, the increase in substrate bias also gives rise to the increase in atom mobility due to an increase in ion energy. The change in film structure from amorphous to crystalline implies the decrease in defect density in the film, leading to the reduction in the extinction coefficient.

5. Conclusion

The properties of zirconium oxide thin film deposited on n-Si(100) and quartz substrates by FCVA were investigated in detail under low pulsed dc substrate bias (0 to −250 V). The results show that both film structure and surface morphology on n-Si(100) are greatly influenced by the substrate bias; in particular, preferred orientation was observed as $V_b$ increased to −250 V. The significant change in surface morphology and film hardness was also related to the changes in the film structure. It was also found that the stoichiometric ratio of the film decreased with $V_b$. For the film on the quartz substrate, nanocrystalline zirconium oxide is only found at $V_b = -250$ V. In addition, the refractive index is increased with $V_b$, while the extinction coefficient and optical band gap $E_g$ are also increased.

Acknowledgments

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