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EPITAXY OF TiO_2 THIN FILM ON SAPPHIRE BY MOCVD*

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EPITAXY OF TiO_2 THIN FILM ON SAPPHIRE BY MOCVD

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ABSTRACT

Epitaxial TiO_2 films have been successfully grown on sapphire substrate at temperatures from 400 to 800°C by thermally decomposing titanium isopropoxide in the presence of O_2 in a cold wall low pressure MOCVD system. Rutile film was grown on sapphire $(11\bar{2}0)$ at 800°C with (101) being the growth plane and $\langle 1\bar{1}0 \rangle$ being parallel to sapphire $\langle 0001 \rangle$. Anatase film was grown on sapphire (0001) at 400°C with (112) being the growth plane and $\langle 1\bar{1}0 \rangle$ being parallel to sapphire $\langle \bar{1}100 \rangle$. The film structure as a function of substrate surface orientation and growth temperature is discussed in detail.

INTRODUCTION

A variety of unique physical properties displayed by a wide range of single crystal oxide materials have been extensively studied and exploited for technological applications. However, very few of these oxide systems have been successfully prepared in the form of thin films which is more suitable for the fabrication of micro devices. Moreover, high quality epitaxial oxide films are the foundation for fabricating novel devices made of multilayer or superlattice configurations which may exhibit new or tailored physical properties. In this work, TiO_2, because of its well understood bulk structure and physical properties, has been selected to study epitaxial film growth in an MOCVD process.

According to the equilibrium phase diagram of the Ti-TiO_2 system [1], stoichiometric TiO_2 has two stable phases, i.e., rutile and anatase at high and low temperatures, respectively. The phase transition temperature is approximately at 750°C; however, various polycrystalline anatase and/or rutile films have been grown on different types of substrates at temperature ranging from 300 to 900°C [2-5]. There was no consensus as for which phase is the stable one as a function of growth temperature. In this work, TiO_2 films were epitaxially grown on sapphire $(11\bar{2}0)$ and (0001) in the temperature range of 400 to 800°C and the results of phases, structure, and epitaxy relationship are presented.

EXPERIMENTAL

The detailed description of our deposition system and sample preparation procedures was presented elsewhere [6]. In brief, our MOCVD apparatus is a cold wall resistance-heated horizontal open flow system with a rectangular shaped quartz reactor. Vapor of the liquid organometallic (OM) precursors, titanium isopropoxide ($Ti(OC_3H_7)_4$, was carried by UHP N_2 gas and pure O_2 was used as oxidant. Except for substrate plane orientation and growth temperature, all the other parameters were fixed as follows: total gas flow rate, 1300 sccm (standard cubic centimeter per min); pressure, 10 Torr; oxygen flow rate, 200 sccm; OM source temperature, 65°C; OM source flow rate, 100 sccm. Typical film thickness is about 2500 Å and growth rates were approximately in the range of 100-150 Å/min. The growth process was believed to be mass transfer limited since the growth rate is sensitive to OM source temperature and flow rate but not deposition temperature. The TiO_2 films were grown on sapphire $(11\bar{2}0)$ and (0001) in the temperature range of 400 to 800°C. The phases and epitaxial structure of the films were examined by X-ray diffraction and Raman scattering. In order to determine whether the film was truly epitaxial and to examine the epitaxial relationship between film and substrate, a four circle X-ray diffractometer was employed. The sample was mounted such that its surface normal was perfectly in parallel with the ϕ angle rotating axis.

RESULTS AND DISCUSSION

TiO_2 on Sa(11$\bar{2}$0)

Figure 1(a) shows the X-ray diffraction spectrum of a film grown on sapphire (11$\bar{2}$0) at 800°C. The data clearly indicate that the film is completely rutile and the growth plane is highly oriented (101) plane ($2\theta = 36.12°$). The four circle X-ray diffraction data indicate that rutile $\langle 0\bar{1}0 \rangle$ was parallel to sapphire $\langle 0001 \rangle$. Rocking curve of rutile (101) plane indicates a mosaic spread (FWHM) of 0.67° as shown in Fig. 1(b). Figure 1(c) shows the ϕ scan (rotating about rutile $\langle 101 \rangle$) of rutile (1$\bar{2}$1) plane which is equivalent to rocking of (0$\bar{1}$0) plane and indicates how the film is laterally aligned with the substrate (FWHM = 3.2°).

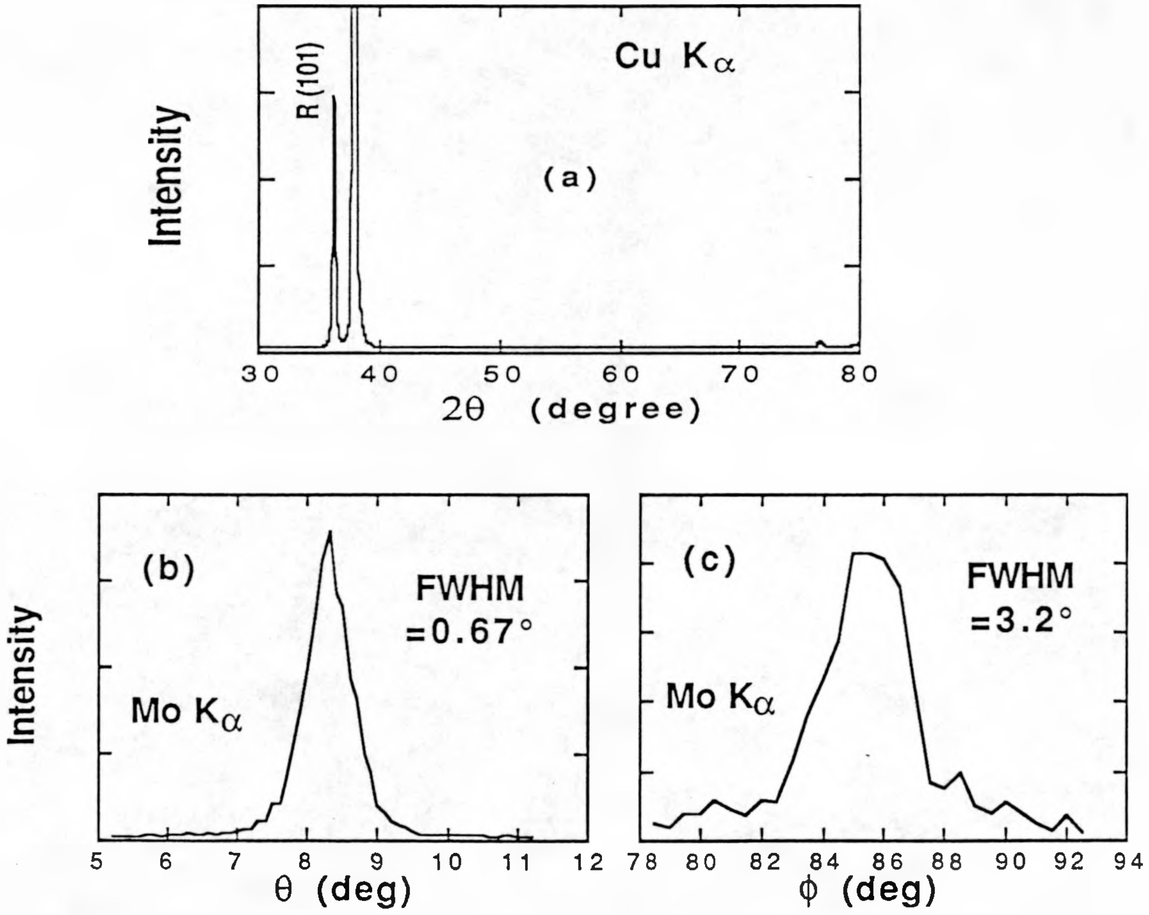

Fig. 1. TiO_2 film (rutile) grown on sapphire (11$\bar{2}$0) at 800°C: (a) X-ray θ-2θ scan data; (b) rocking curve of (101) growth plane; (c) ϕ scan of (1$\bar{2}$1) plane.

A series of films were grown on sapphire (11$\bar{2}$0) at temperatures ranging from 400 to 700°C and their X-ray θ-2θ scan data are shown in Fig. 2. As can be seen, at 700°C the film remains rutile; however, as temperature further decreased to 600°C, the rutile (101) peak became very weak and another peak (2θ = 39.24) which was due to rutile (200) began to emerge. This trend seemed to become more obvious at 500°C, and at 400°C the spectrum became dominated by one strong single peak again, but the 2θ value (39.45) was substantially different from that of any rutile or anatase plane. Since this film structure (400°C) could not be determined from X-ray data, Raman scattering was used to identify the phase and the spectrum is shown in Fig. 3. We attribute the two film peaks (613 and 443 cm^{-1}) to rutile (611 and 447 cm^{-1}) [7] and suggest that the shifting and broadening of the peaks are probably due to a distortion of the rutile film. This seems to be in agreement with the X-ray data which also show a deviation of 2θ. Therefore, the 400°C film is probably a distorted rutile film.

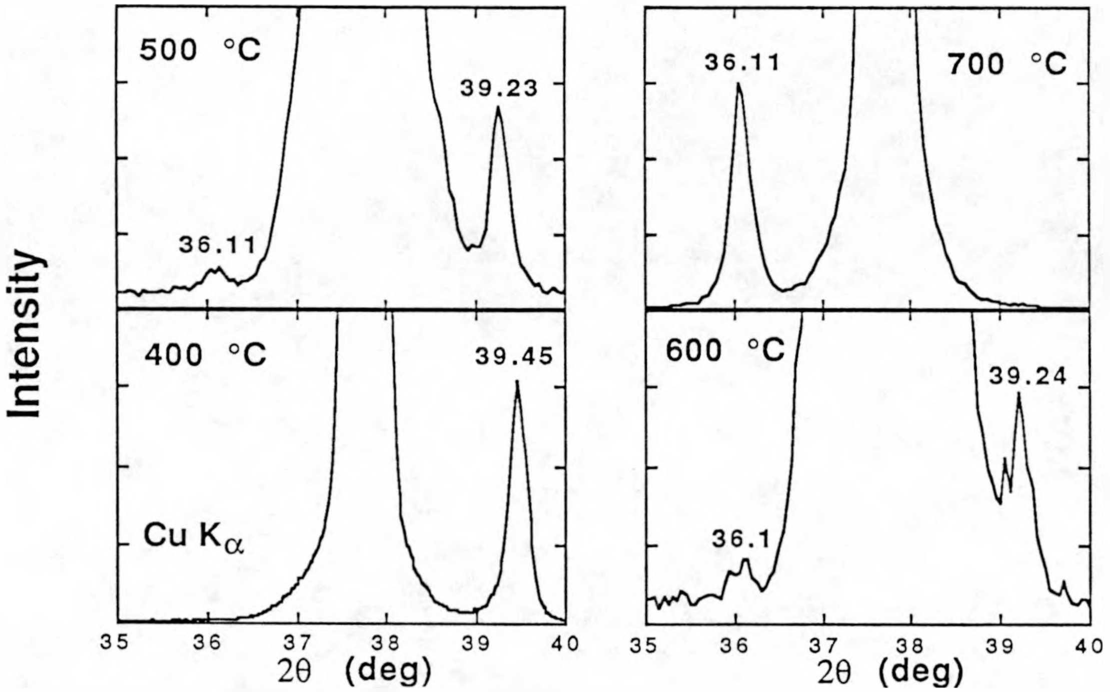

Fig. 2. X-ray θ-2θ scan data of TiO_2 films grown on sapphire (11$\bar{2}$0) at temperatures: (a) 700°C, (b) 600°C, (c) 500°C, (d) 400°C.

TiO_2 on Sa(0001)

The X-ray diffraction spectrum of a film grown on sapphire (0001) at 400°C is shown in Fig. 4(a). The data indicate a highly oriented film with the growing plane being anatase (112). Furthermore, from the four circle X-ray measurement, anatase ⟨1$\bar{1}$0⟩ was found to be parallel to sapphire ⟨$\bar{1}$100⟩. The rocking curve of anatase (112) plane and ϕ scan of (004) plane (equivalent to rocking of (1$\bar{1}$0) plane) are shown in Fig. 4(b) and (c), respectively.

A series of films were grown on sapphire (0001) at temperatures ranging from 500 to 800°C to explore the film structure transition. The X-ray θ-2θ scan data of this series of samples are shown in Fig. 5. As can be seen, at 500°C the film is still dominated by anatase (112), but another peak (probably anatase (004)) began to appear. At 600°C the film was composed of three comparable peaks

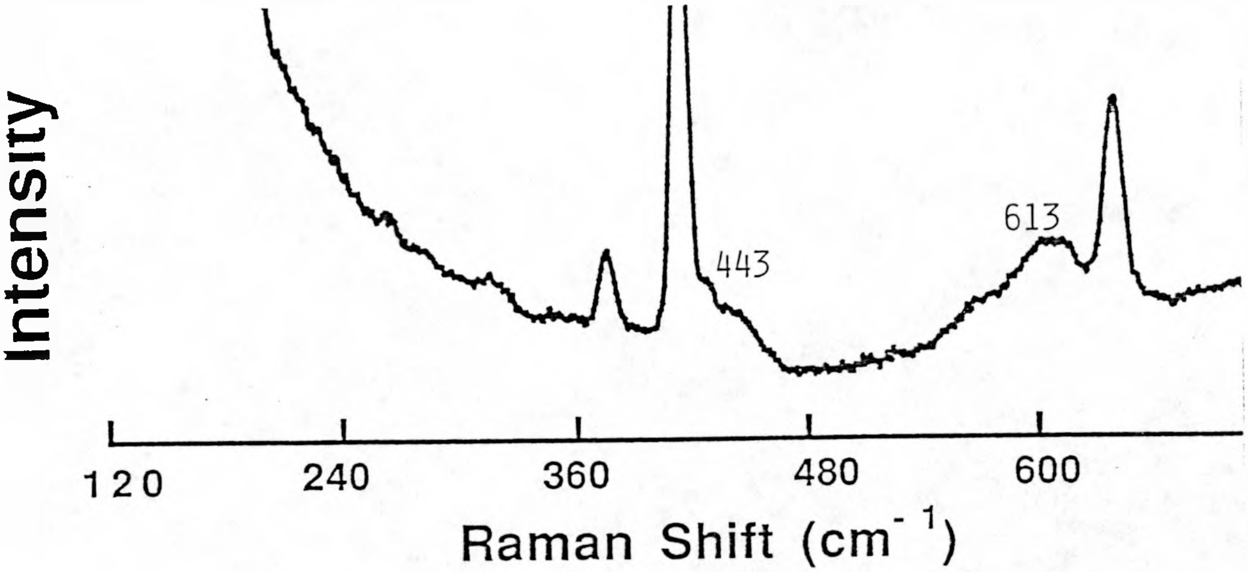

Fig. 3. Raman spectrum of the TiO_2 film on sapphire (11$\bar{2}$0) grown at 400°C.

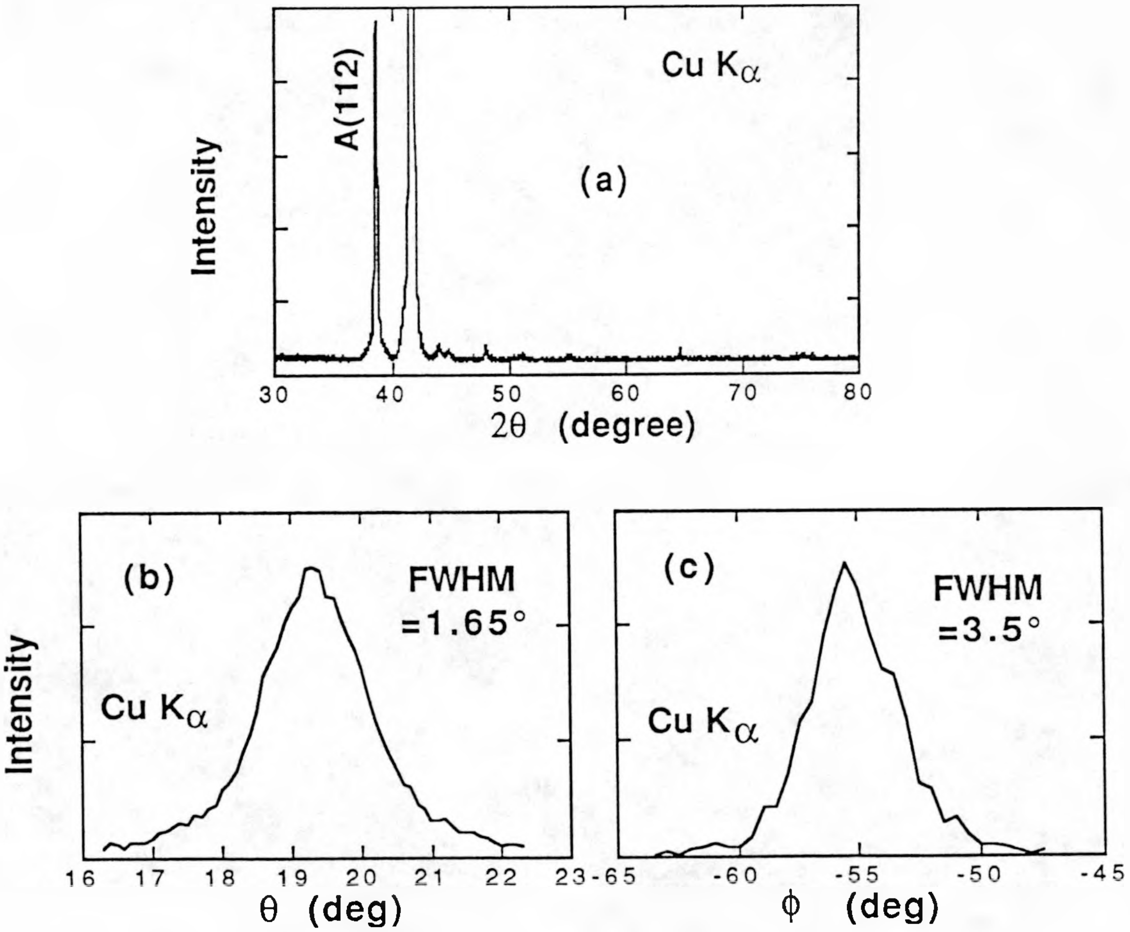

Fig. 4. TiO_2 film (anatase) grown on sapphire (0001) at 400°C: (a) X-ray θ-2θ scan data; (b) rocking curve of (112) growth plane; (c) ϕ scan of (004) plane.

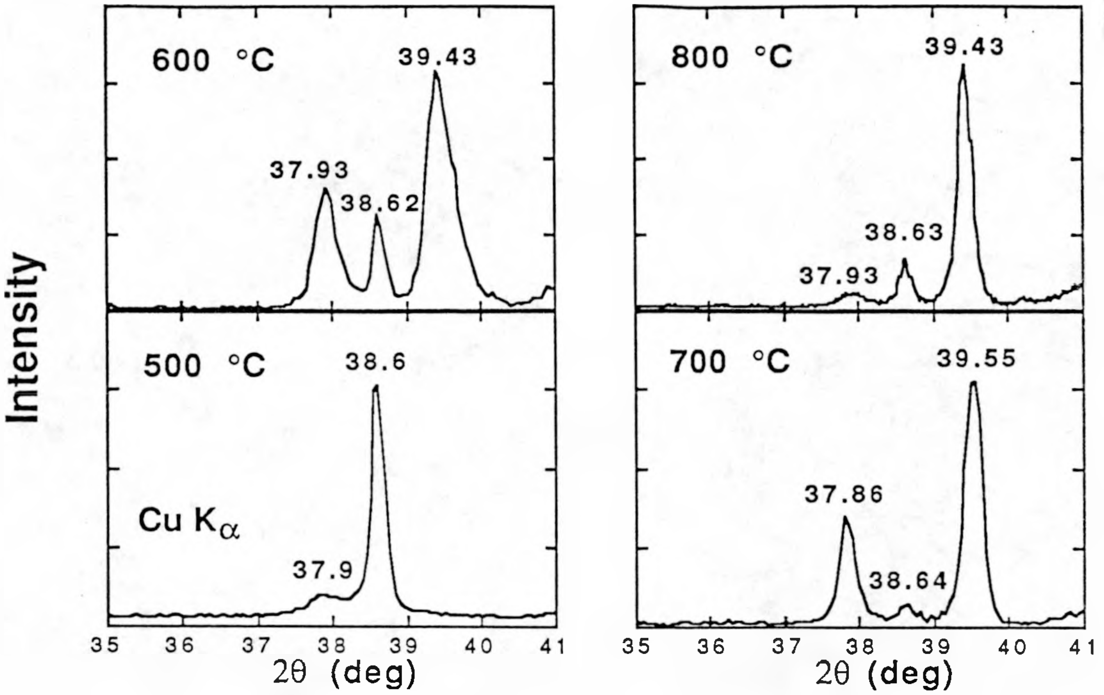

Fig. 5. X-ray θ-2θ scan data of TiO_2 films grown on sapphire (0001) at temperatures: (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C.

including anatase (112) and (004); however, the strongest peak could not be identified. The 700°C film shows similar spectrum with further reduced intensity of anatase (112). As temperature increased to 800°C, the film was dominated by the peak with $2\theta = 39.43°$. The Raman spectrum of the 800°C film did show a characteristic anatase signature; however, the intensity of the spectrum was much weaker than the 500°C film which may correspond to the small amount of anatase as shown in Fig. 5(d). The structure of the phase with $2\theta = 39.43°$ has not been resolved at the present time.

CONCLUSION

Epitaxial TiO_2 films have been successfully grown on sapphire substrates in the temperature range of 400 to 800°C by thermally decomposing titanium isopropoxide in the presence of O_2 in a cold wall low pressure MOCVD system. The phases and structure of deposited films depended strongly on substrate surface orientation and growth temperature with the former playing a more important role. Rutile films were invariably obtained on sapphire (11$\bar{2}$0) irrespective of growth temperature. However, the film grown at 800°C was a single domain crystal with a well defined epitaxy relationship. As the growth temperature decreased the film began to contain two different domains (growth planes) and eventually recovered to a single domain at 400°C, as distorted rutile. On the other hand, single domain anatase was formed on sapphire (0001) at 400°C with a well defined epitaxy relationship. But as the growth temperature increased, the film began to develop into three different domains and eventually, at 800°C, recovered to one dominating domain again; however, the phase and structure of this crystal is unknown.

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