Growth of a High Quality Quartz Film on Sapphire by Catalyst-Enhanced Atmospheric-Pressure Vapor-Phase Epitaxy Using Buffer Layers

Naoyuki Takahashi,*,† Jun Majima,† Takato Nakumura,† Satoshi Nonaka,‡ Hiromi Yagi,‡ Yoichi Shinriki,‡ and Katsumi Tamanuki‡

Department of Materials Science and Technology, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatus, Shizuoka 432-8561, Japan, and Humo Laboratory Company, 5-9-11 Nishiogi-Kita, Suginami-ku, Tokyo 167-0042, Japan

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Quartz films (SiO_2 with hexagonal structure) are grown on a sapphire (0001) substrate by atmospheric-pressure vapor-phase epitaxy using quartz buffer layers. The full width at half-maximum (fwhm) of the X-ray (0003) diffraction peak for the quartz films with the buffer layer was found to be smaller than that of the quartz film without a buffer layer. The homogeneous in-plane alignment of the epitaxially grown quartz was confirmed by X-ray pole figure analysis. A smooth surface with roughness of less than 5 nm was obtained with a quartz buffer layer. The refractive index of the quartz epitaxial films with a quartz buffer layer was 1.538.

Introduction

High quality quartz has been widely applied for electronic equipment such as oscillators, vibrators, surface acoustic wave devices, and optical waveguides. Conventionally, single crystals of quartz have been grown hydrothermally at high temperature under high pressure.[1,2] It takes a very long time to synthesize the crystals large enough for industrial applications. It is also difficult to prepare the quartz crystals with arbitrary shapes such as film and fiber, so that further processing is essential to make the desired shapes of quartz. Furthermore, for oscillators, vibrators, and filters, thin films have been used as a standard high-frequency source (or wave source). However, thinning a large crystal to thin film by physical processing such as cutting and polishing limits the thickness to 50 μm. Furthermore, though the vapor phase growth of SiO_2 thin films has been reported in great numbers,[3−10] the vapor phase growth of quartz thin films is not reported. Therefore, an alternative growth technique should be developed to obtain high quality quartz films applicable to higher frequency devices.

In a previous paper, we reported that quartz epitaxial film is successfully grown on a sapphire (0001) substrate by catalyst-enhanced vapor-phase epitaxy under atmospheric pressure.[11] The obtained quartz films showed a minimum full width at half-maximum (fwhm) of the X-ray (0003) peak of 600 s. However, this fwhm is larger than that (180 s) of the bulk quartz prepared by hydrothermal synthesis. Therefore, further improvement (to fwhm lower than 180 s) is required to obtain the quartz films by catalyst-enhanced vapor-phase epitaxy under atmospheric pressure for practical application. In the present paper, therefore, we report the results of the epitaxial growth of quartz using a buffer layer on sapphire (0001) substrate.

Experimental Section

Quartz films were grown by atmospheric-pressure vapor-phase epitaxy (AP-VPE) using $Si(OC_2H_5)_4$ (99.99%) and O_2 (99.999%) as starting materials in the presence of gaseous HCl. The setup used in the present study was described previously.[11] Growth of the hexagonal quartz epitaxial layer was carried out in a vertical glass reactor under atmospheric pressure. Optical grade polished sapphire of 10 × 10 mm with the (0001) orientation (c face) was used as a substrate. The misorientation was within ±0.5°. The substrate was degreased by successive cleaning in acetone and deionized water and then chemically etched with a solution of H_3PO_4/H_2SO_4 (1:3) at 433 K for 600 s before being dried in a stream of dry nitrogen. Afterward, the sapphire substrate was placed on the susceptor in the reactor. $Si(OC_2H_5)_4$ was transported to the reactor with N_2 as a carrier gas bubbling through the $Si(OC_2H_5)_4$ solution, which was kept at 343 K. Simultaneously, gaseous HCl as a catalyst was supplied to facilitate the decomposition of $Si(OC_2H_5)_4$.

Figure 1 shows a typical quartz growth process using a quartz buffer layer. It has two steps. The buffer layer of quartz was deposited at 773 K and then the epitaxial film was grown at 843 K. At the first step, the buffer layer was annealed at 843 K for 600 s under O_2 flowing atmosphere. The buffer layer

* To whom correspondence should be addressed. E-mail: tntakah@ipc.shizuoka.ac.jp. Tel/Fax: +81-53-478-1197.
† Shizuoka University.
‡ Humo Laboratory Company.

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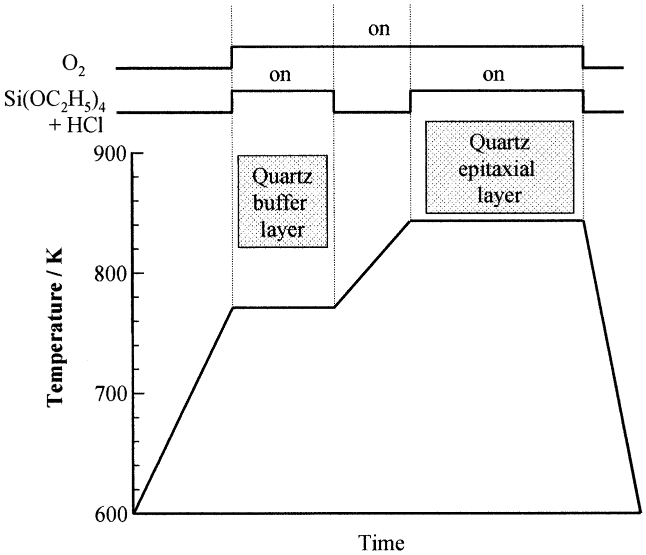

Figure 1. Time chart of the growth process by AP-VPE using the quartz buffer layer.

Table 1. Typical Growth Conditions

$Si(OC_2H_5)_4$ partial pressure	3.34×10^2 Pa
O_2 partial pressure	3.34×10^4 Pa
HCl partial pressure	1.69×10^2 Pa
$Si(OC_2H_5)_4$ source temperature	343 K
total pressure	1.01×10^5 Pa
carrier gas	N_2
total flow rate	1.33×10^{-5} m^3s^{-1}
growth temperature of quartz buffer layer	773 K
growth temperature of quartz epitaxial layer	843 K

was amorphous. At the second step, the epitaxial quartz layer was started again by supplying $Si(OC_2H_5)_4$, O_2, and HCl to the reactor. Typical growth conditions are summarized in Table 1. To elucidate the effect of quartz buffer layer, the same experiments were also carried out without the buffer layer.

The crystallinity of the quartz films was assessed by X-ray diffraction (XRD; Rigaku Co., RINT2000) analysis and XRD pole figure (Rigaku Co., ATX-G) analysis. The thickness and surface morphology of the films were evaluated by means of scanning electron microscopy (SEM) (Shimadzu superscan) and atomic force microscopy (AFM; shimadzu Co., SPM-9500), respectively. The refractive index of the films was measured using a Mizojiri-kougaku DHA-OLX7 ellipsometer at a wavelength of 633 nm. XPS spectra were measured using a Shimadzu XRTOS-XSAM 800 X-ray photoelectron spectrometer. All the measurements were performed using films of approximately 1.0 μm thickness.

Results and Discussion

Figure 2 shows the fwhm of the (0003) diffraction line for the obtained hexagonal quartz films as a function of the thickness of the quartz buffer layer on sapphire (0001). As is evident from Figure 2, the fwhm decreases with increasing thickness of the buffer layer up to 50 nm and then gradually increases. A minimum fwhm value of 90 s is obtained for the buffer layer thickness of approximately 50 nm. This value is comparable to that (180 s) of the epitaxial quartz layer deposited by hydrothermal synthesis, implying that the optimum thickness of the buffer layer is around 50 nm.

Representative X-ray pole figures of the quartz film with a quartz buffer layer of 50-nm thickness and of a quartz film without a buffer layer are shown in Figure 3. The X-ray pole figure is available from the quartz $(10\bar{1}1)$ reflection ($2\theta = 26.65°$) for a quartz film grown on sapphire substrate. The hexagonal quartz crystal with a *c*-axis orientation has 6-fold symmetry. Thus, six

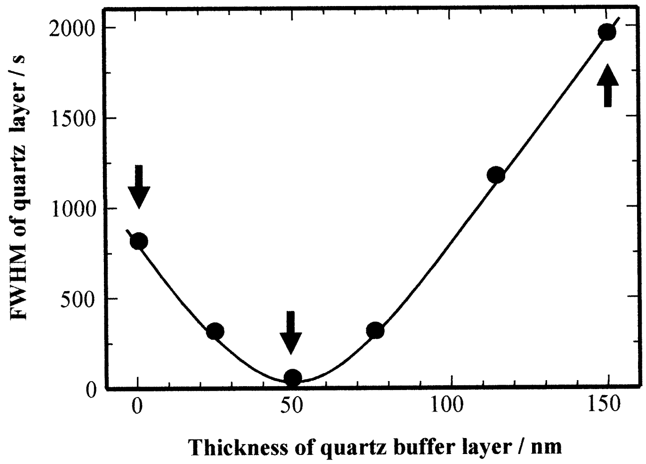

Figure 2. Fwhm value of X-ray peak of the (0003) hexagonal quartz as a function of the thickness of a quartz buffer layer on sapphire (0001).

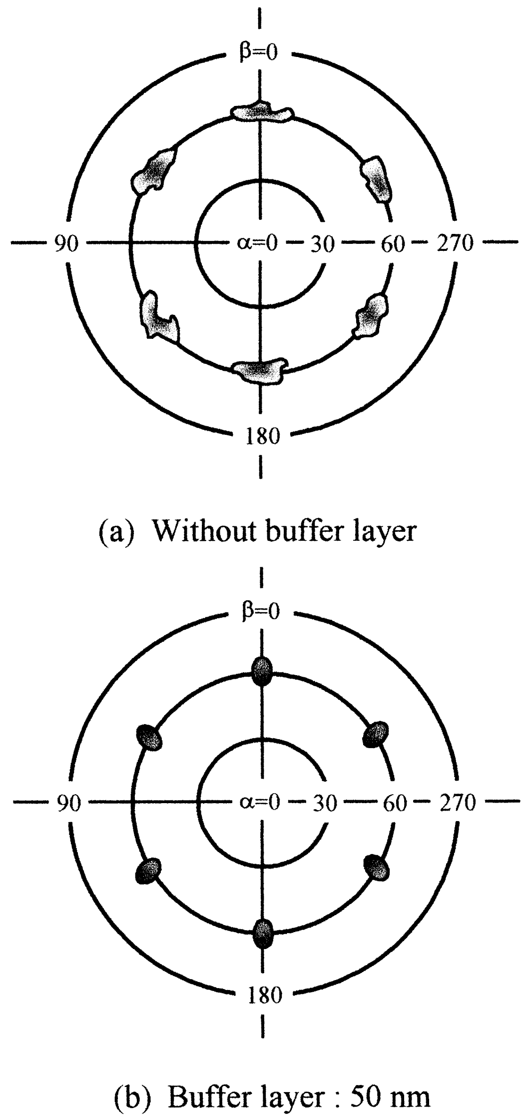

Figure 3. Pole figure of (a) the quartz film without buffer layer and (b) the quartz film with buffer layer of 50 nm. Stereographic projection of X-ray pole figure result for the quartz $(10\bar{1}1)$ reflection ($2\theta = 26.65°$) for a quartz film grown on sapphire substrate.

poles should appear in the pole figure if it has a homogeneous in-plane alignment. The six poles were not found on the X-ray pole figure for the quartz films

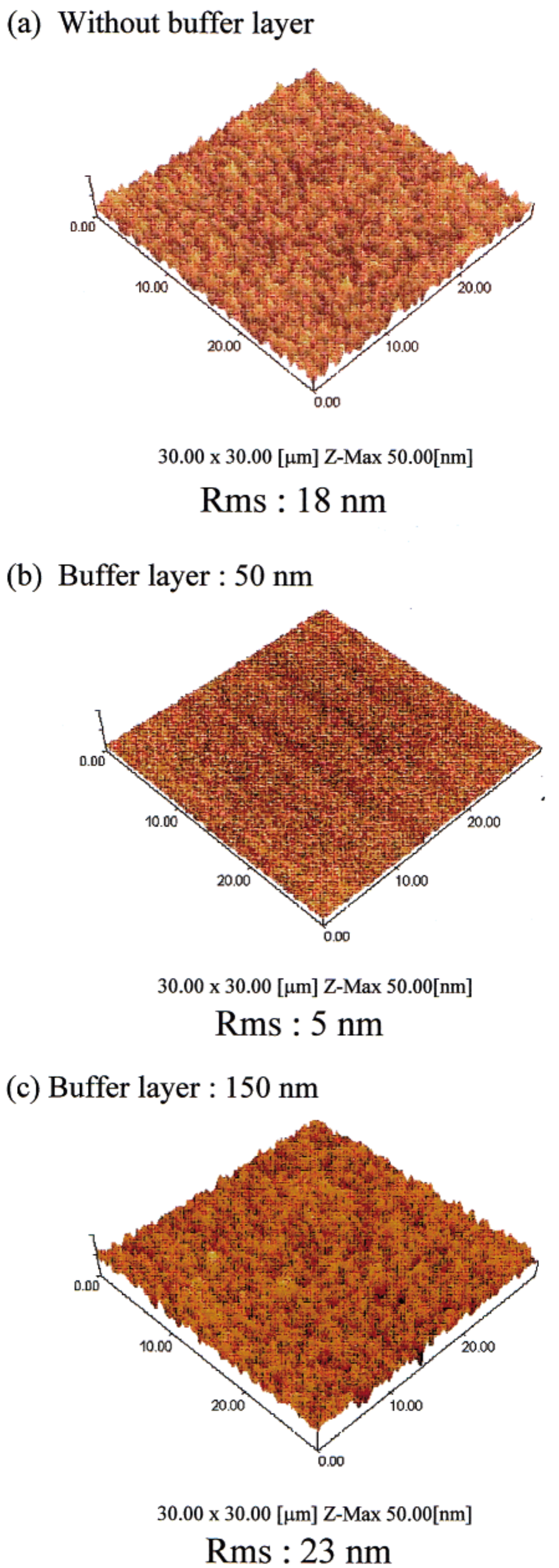

Figure 4. AFM image of the quartz epitaxial layer. Thicknesses of quartz buffer layers are (a) 25 nm, (b) 50 nm, and (c) 150 nm.

without the buffer layer. On the other hand, the six poles separated by angles of 60° were found clearly for the quartz films with the buffer layer, and evidence that the *c*-axis is perpendicular to the film. Also, this finding supports the homogeneous in-plane alignment of the epitaxially grown quartz film.

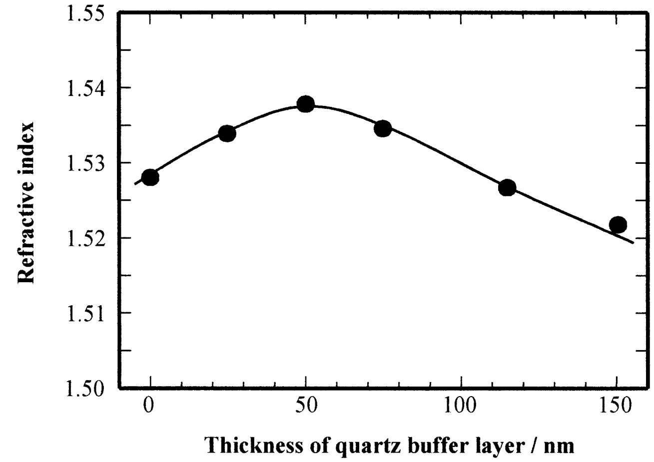

Figure 5. Refractive index for the obtained hexagonal quartz films as a function of the thickness of the quartz buffer layer on sapphire (0001).

Figure 4 shows the AFM images of the quartz epitaxial layer indicated by arrows in Figure 2. As is shown in Figure 4(b), a smooth surface with roughness of less than 5 nm is obtained when the quartz buffer layer of 50 nm is present. In the presence of quartz buffer layers of 25 and 150 nm, they showed very rough surfaces. It is therefore evident that the surface morphology is significantly affected by the quartz buffer layer.

Figure 5 shows the refractive index for the obtained hexagonal quartz films as a function of the thickness of the quartz buffer layer on sapphire (0001). As is evident from Figure 5, the refractive index increases with increasing thickness of the buffer layer up to 50 nm and then gradually decreases. A minimum refractive index value of 1.538 is obtained for the buffer layer thickness of approximately 50 nm. This value is comparable to that (1.54) of the epitaxial quartz layer deposited by hydrothermal synthesis,[12,13] implying that the optimum thickness of the buffer layer is around 50 nm. XPS analysis confirmed that the C and Cl percentages in the quartz film prepared in this study were below 1 at. % (the identification limit).

The effect of the quartz buffer layer has been investigated for the epitaxial growth of quartz by AP-VPE. X-ray diffraction, X-ray pole figure, AFM, and refractive index observations indicate that the optimum thickness of the quartz buffer layer is 50 nm.

Conclusion

A hexagonal quartz epitaxial layer of good quality is obtainable by prior deposition of a quartz buffer layer. The key growth parameters are the deposition temperature and the annealing temperature of the quartz buffer layer. In future research, we will concentrate on the improvement of crystallinity by optimization of the buffer layer in order to grow the quartz films.

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