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Catalyst-enhanced vapor-phase epitaxy of quartz thin films under atmospheric pressure

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Preparation of quartz (rock crystal) films has been studied by an atmospheric pressure chemical vapor deposition method using $Si(OC_2H_5)_4$ and O_2 as starting materials in the presence of gaseous HCl. The films were deposited onto a sapphire (0001) substrate at 600–850 °C with a growth rate of 0.3–3.0 μm h^{-1}. Their X-ray diffraction profiles showed an intense diffraction peak at 50.6° assigned to the (0003) diffraction of quartz with a hexagonal structure suggesting epitaxial growth. The full-width at half-maximum was 10.0 min for the quartz film prepared at 850 °C. Reflection high-energy electron diffraction measurements showed a diffraction pattern similar to that of a single crystal of quartz. It was found by energy-dispersive analysis of the X-rays that the [O]/[S] ratios of the deposited films were in the range of 1.94–1.97, independent of the growth temperature. Fourier transform infrared spectra exhibited a weak absorption band at 3585 cm^{-1}, suggesting OH radicals to be present as an impurity. The refractive index of the quartz epitaxial films prepared at 850 °C was 1.528.

1. 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] However, it takes a very long time to synthesize crystals large enough for industrial applications. Also, it is difficult to prepare quartz crystals with arbitrary shapes such as films and fibers, so that further processing is essential to make various 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 a thin film by physical processing such as cut and polish is limited up to 50 μm in thickness. Furthermore, though examples of the vapor phase growth of SiO_2 thin films have been reported in great numbers up to now,[3–10] the vapor phase growth of quartz thin films has not been reported. Therefore, an alternative growth technique needs to be developed in order to obtain high quality quartz films applicable for higher frequency devices.

For this reason, we have examined a new method using $Si(OC_2H_5)_4$ and O_2 as starting materials. From a technological viewpoint, this has several advantages over the hydrothermal method of preparation: (a) direct growth of the thin film is feasible by the reaction of a simple alkoxide, $Si(OR)_4$, with O_2 under atmospheric pressure; (b) such alkoxides with high purity are commercially available. (c) post-annealing is not necessary; (d) the growth rate is as fast as that of the conventional SiO_2 vapor phase deposition despite the fact that the resulting films are of high quality.[11]

2. Experimental

Quartz films were grown by atmospheric pressure vapor-phase epitaxy (AP-VPE) using $Si(OC_2H_5)_4$ and O_2 as starting materials in the presence of gaseous HCl. The purities of the $Si(OC_2H_5)_4$ and O_2 used were 99.999%, respectively. The set-up used in the present study is illustrated in Fig. 1. Growth of the hexagonal quartz epitaxial layer was carried out in a vertical quartz reactor under atmospheric pressure. An 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 mixed solution of H_3PO_4–H_2SO_4(1 : 3) at 160 °C for 10 min before being dried in a stream of dry nitrogen. Afterwards, the sapphire substrate was placed on the susceptor in the reactor. $Si(OC_2H_5)_4$ was transported into the reactor with N_2 as a carrier gas bubbling through the $Si(OC_2H_5)_4$ solution kept at 70 °C. Simultaneously, gaseous HCl as a catalyst was supplied in order to facilitate the decomposition of $Si(OC_2H_5)_4$. Typical growth conditions are summarized in Table 1.

The crystallinity of the quartz films was assessed both by double-crystal X-ray diffraction analysis and by the reflection high-energy electron diffraction (RHEED) technique. The film thickness and surface morphology were evaluated by means of scanning electron microscopy (SEM; Shimadzu superscan) and atomic force microscopy (AFM; Shimadzu Co., SPM-9500), respectively. The chemical composition of the films was determined by energy-dispersive analysis of X-rays (EDAX) using a JEOL Ltd. JXA-8900R instrument, in which the data were calibrated with a quartz single crystal of known stoichiometry. Fourier transformed infrared (FT-IR) measurements were carried out using a Shimadzu FTIR-8000 infrared spectrometer. The refractive index of the films was measured using a Mizojiri-kougaku DHA-OLX7 ellipsometer at a wavelength of 633 nm. Quartz thin films of 1 μm thickness were used in the measurements.

3. Results and discussion

Fig. 2 shows a typical X-ray diffraction profile of the film deposited at 850 °C. It is apparent that an intense diffraction

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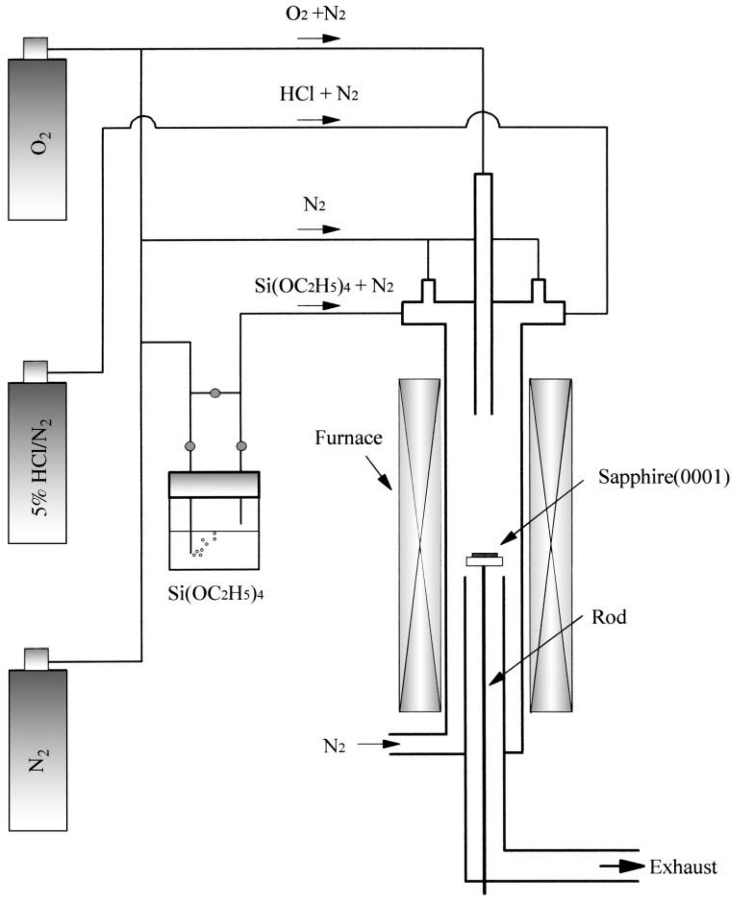

Fig. 1 Schematic diagram of the apparatus used in this work.

Table 1 Typical growth conditions

$Si(OC_2H_5)_4$ partial pressure	3.3×10^{-3} atm
O_2 partial pressure	3.3×10^{-1} atm
HCl partial pressure	1.67×10^{-3} atm
Total pressure	1 atm
Carrier gas	N_2
Total flow rate	800 cm^3 min^{-1}
Growth temperature	600–850 °C
Duration of deposition	1 h

peak appearing at 50.6° is assigned to the (0003) diffraction of quartz with a hexagonal structure. Another peak at 41.8° is due to the (0006) diffraction of the sapphire substrate. This implies that the quartz films were grown epitaxially under atmospheric pressure using $Si(OC_2H_5)_4$ and O_2. The lattice constant was calculated to be $c = 5.413$ Å utilizing the observed (0003) diffraction, which is slightly larger than reported value of 5.393 Å.[12] This is probably due to the lattice mismatch between quartz and sapphire.

In Fig. 3, the growth rate of the quartz film is plotted as a function of the growth temperature. As the temperature is increased from 600 to 850 °C, the rate increases exponentially from 0.4 to 3.0 μm h^{-1}. The activation energy was calculated to be approximately 16.7 kcal mol^{-1} from the slope of the growth rate against the inverse of the growth temperature in K^{-1}. Stonnington *et al.* reported that for the growth of SiO_2 film using $Si(OC_2H_5)_4$ and O_2 without any catalyst, the activation energy was 55.0 kcal mol^{-1}, which is about 4.5 times higher than that obtained in this study.[11] This means that HCl plays

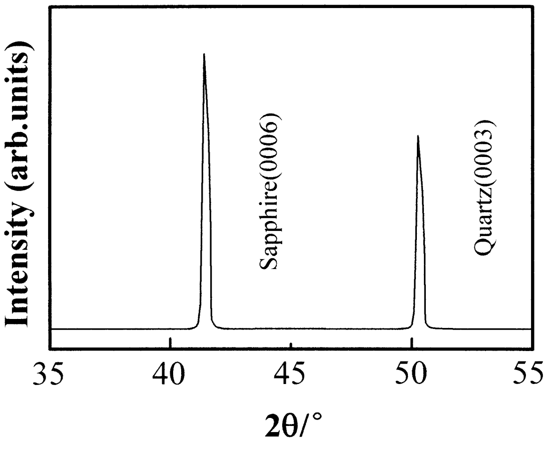

Fig. 2 X-ray diffraction pattern of the quartz film deposited at 850 °C.

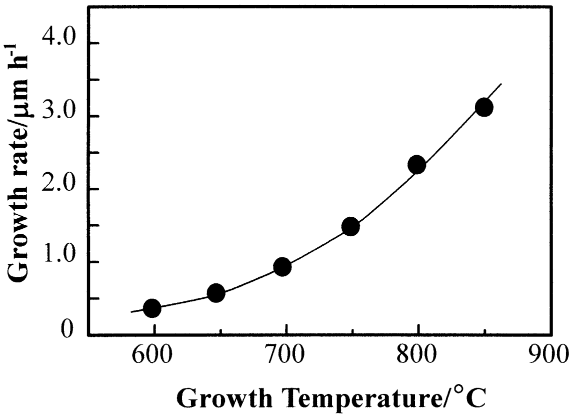

Fig. 3 Plots of the growth rate of quartz films as a function of growth temperature.

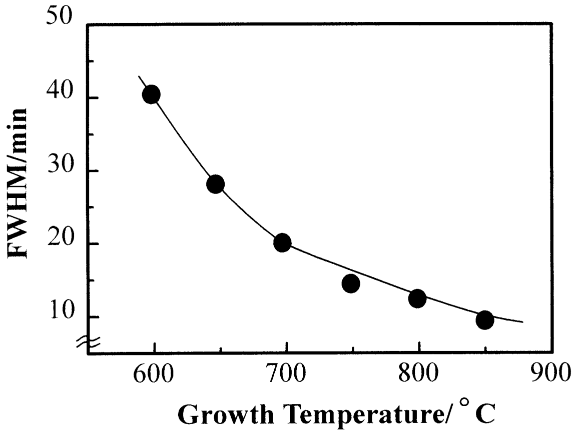

Fig. 4 The FWHM value of the (0003) X-ray diffraction peak of hexagonal quartz film as a function of the growth temperature.

an important role in the growth of the quartz film from $Si(OC_2H_5)_4$ and O_2 under atmospheric pressure. Therefore, the present system of $Si(OC_2H_5)_4$–O_2 in the presence of gaseous HCl is of promise for the growth of quartz films with high growth rates.

Fig. 4 shows the plot of FWHM of the (0003) diffraction line for the obtained hexagonal quartz films as a function of the growth temperature. As is evident from Fig. 4, the FWHM decreases with increasing growth temperature up to 850 °C. A minimum FWHM value of 10.0 min was obtained at a growth temperature of 850 °C. This value is large compared with that (2.5 min) of quartz prepared by hydrothermal methods.

A representative RHEED for the deposited quartz film at 850 °C is shown in Fig. 5. It is immediately noticed that the RHEED pattern shows spots, indicating that the grown layer is of good crystallinity.

Fig. 6 shows a representative AFM image of the quartz film deposited at 850 °C. As is shown in Fig. 6, a smooth surface with roughness less than 20 nm was obtained. For the application of the quartz film to devices, it needs to have a roughness of less than µm order. It is therefore evident that quartz films grown epitaxially by AP-VPE satisfy the demands.

The composition of the epitaxially grown quartz films was assayed by EDAX measurements, in which C and Cl were not detected in the samples prepared in this study. It is found that the [O]/[Si] ratio is constant at 1.94–1.97, being independent of the growth temperature. The slight deviation from stoichiometry may imply the formation of oxygen vacancies in the epitaxial layer.

It is known that the optical properties of quartz detoriate due to the incorporation of OH radicals.[13] Fig. 7 shows the FT-IR spectrum of the epitaxially grown quartz film at 850 °C. The FT-IR spectrum of the quartz epitaxial layer in this study is comparable to that of quartz prepared by the hydrothermal method. A weak signal is observed at 3585 cm^{-1}, assigned to the stretching mode of the OH radical. The peak of this signal increased when the temperature was lower than 850 °C. The refractive index was approximately 1.528 for the epitaxially grown quartz film at 850 °C. This value is rather low compared with that (1.54) for the hydrothermally prepared quartz crystals.[14,15] Consequently, further improvement is in progress on the crystalline quality.

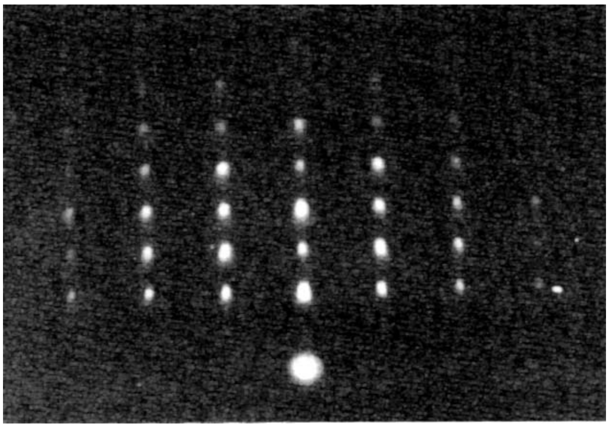

Fig. 5 RHEED pattern of quartz film.

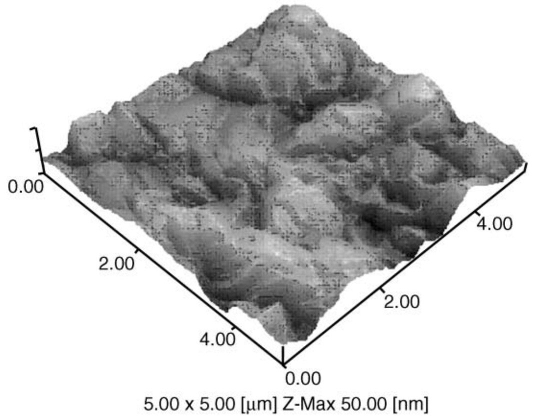

Fig. 6 AFM image of the quartz film deposited at 850 °C.

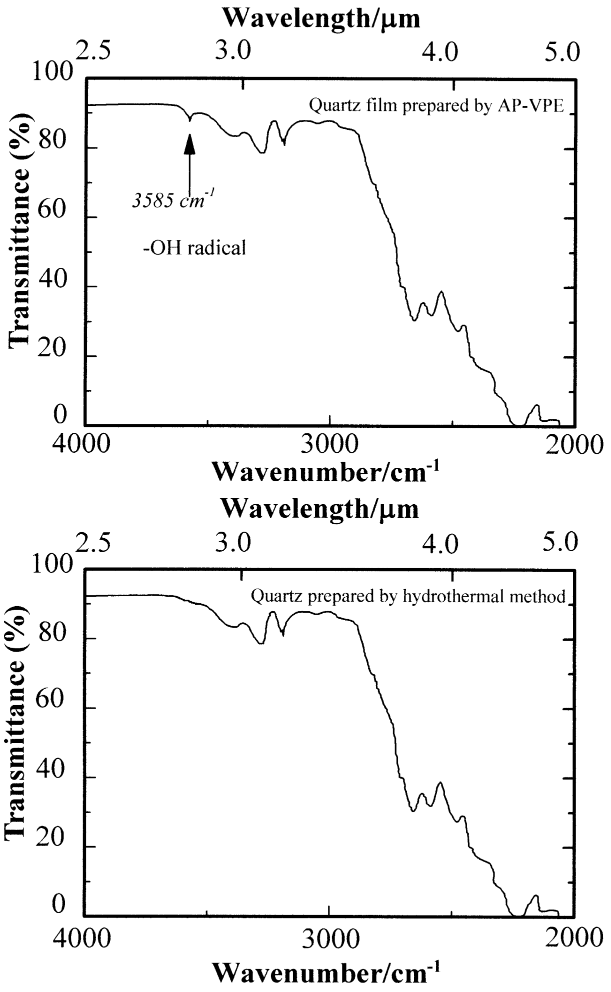

Fig. 7 FT-IR spectra of the deposited quartz film at 850 °C and quartz prepared by the hydrothermal method.

4. Conclusions

Thin films of quartz were deposited onto the sapphire (0001) substrate under atmospheric pressure by a new vapor-phase epitaxy using $Si(OC_2H_5)_4$, O_2 and HCl as source materials. Deposited films prepared in the temperature range of 600 to 850 °C showed an X-ray diffraction pattern typical of quartz with a hexagonal structure, suggesting epitaxial growth. The minimum FWHM of the (0003) diffraction and the maximum growth rate, 10.0 min and 3.0 μm h^{-1}, respectively, were observed at 850 °C. The RHEED measurements showed a diffraction pattern similar to that of a single crystal, confirming that the quartz films had grown epitaxially. It was found by the EDAX analysis that the deposited films have an [O]/[Si] ratio of 1.94–1.97, which is independent of the growth temperature. The refractive index of the quartz epitaxial layers was 1.528. Consequently, it is evident that the reaction of $Si(OC_2H_5)_4$ with O_2 in the presence of gaseous HCl under atmospheric pressure yields epitaxial growth of quartz films onto the sapphire (0001) substrate with rapid growth rate.

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