Growth of Quartz Thin Films by Catalyst-Enhanced Vapour-Phase Epitaxy under Atmospheric Pressure

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***Abstract*—Preparation of quartz films by means of catalyst-enhanced chemical vapour deposition utilizing the reaction between $Si(OC_2H_5)_4$ and O_2 in the presence of gaseous HCl is summarized.**

I. INTRODUCTION

Quartz is of piezoelectric and has been widely used for a variety of electronic devices. Conventional route to prepare the oscillators involves crystal growth of quartz with a hydrothermal method which takes for a few months to obtain large crystals, followed by further processing such as cut and polish in order to get thin quartz plates with appropriate thickness and crystal orientation. This technique is based on a hydrothermal synthesis of quartz crystal using seed crystals developed by Spezia in 1905.

As for the growth of quartz by means of chemical vapour deposition, however, no report has been found except for ours although there are a large number of reports on the growth of the SiO_2 thin films. In this paper, therefore, the preparation of quartz thin films by means of catalyst-enhanced chemical vapour deposition utilizing the reaction between $Si(OC_2H_5)_4$ and O_2 is summarized [1-3].

II. EXPERIMENTAL

Quartz films were grown by a vapour-phase exitaxy technique under atmospheric pressure utilizing the reaction $Si(OC_2H_5)_4$ and O_2 in the presence of gaseous HCl as a catalyst. Source materials of $Si(OC_2H_5)_4$ and O_2 used were of 99.999% purity. The set-up used in this study is illustrated in Fig.1. Growth of the hexagonal quartz films were carried out in a vertical glass reactor under atmospheric pressure. Polished sapphire substrates of 10 x 10 mm with the (0001) (C-face) and the $(1\bar{1}\bar{2}0)$ (A-face) surfaces were used. The substrate was degreased by successive cleaning in acetone and deionised water and then chemically etched with a mixed solution of H_3PO_4-H_2SO_4 (1 : 3) at 60 º for 10 min before being dried in a stream of dry N_2. Afterwards the sapphire substrate was placed on the susceptor at the top of the glass rod 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 ºC. Simultaneously, gaseous HCl was supplied in order to facilitate the decomposition of $Si(OC_2H_5)_4$.

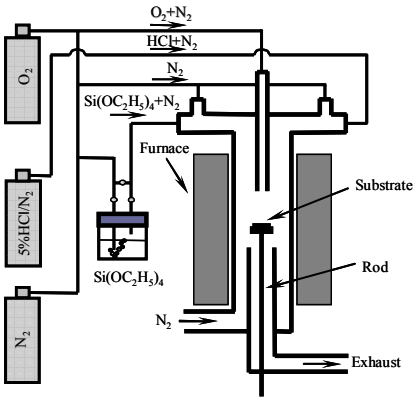

Figure 1 Schematic diagram of the set-up used in this study

The crystallinity of the quartz films was assessed by a Rigaku RINT200 X-ray diffractometer. XRD pole figure analysis was carried out using Rigaku ATX-G diffractomenter to elucidate the in-plane alignment of the films. The film thickness and surface morphology were evaluated with a Shimadzu superscan SEM microscope and a Shimadzu SPM-9500 AFM microscope, respectively. Raman spectra were measured using a Dilor Super Labram spectrometer by exciting the samples with a light of 524.5 nm of Ar^+ laser. Synchrotron-based luminescence measurements were carried out at Daresbury Synchrotron, both on beamlines 3.2 (5 - 30 eV) and MPW6.1 (40 - 440 eV). These two beamlines allowed the band-edge structure and core level Si *L*-edges to be probed respectively. In each case, the mobile luminescence end-station was used, with either broad-band or monochromatic luminescence detection [4].

III. RESULTS AND DISCUSSION

A. Growth of Quartz Thin Films on Sapphire(0001) Surface

It has been well known that the quartz is one of the polymorphs of SiO_2 stable below 573 ºC, implying that the crystal growth should be carried out below the temperature. $Si(OC_2H_5)_4$ used in this study is one of the popular source

materials for the preparation of SiO_2 films both by sol-gel process and by chemical vapour deposition although its thermal decomposition in an dry atmosphere occurs at high temperature more than 1000 ºC. This means that the presence of a catalyst to lower the decomposition temperature is essential for the growth of quartz films. It was found by preliminary experiments the fact that gaseous HCl facilitates the decomposition of $Si(OC_2H_5)_4$ at low temperature.

The films with 30 μm thickness were grown on sapphire $(11\bar{2}0)$ surface at 570 ºC for 1 hr under the conditions of the partial pressures of $Si(OC_2H_5)_4$, O_2 and gaseous HCl were 3.34 x 10^2, 3.34 x 10^4, 1.01 x 10^2 Pa, respectively. Total flow rate was 1.33 x 10^{-5} m^3 s^{-1}.

In the XRD profile of the as-deposited film a strong diffraction line was observed at 50.6º assigned to the (003) diffraction of the quartz with hexagonal structure, suggesting that the quartz films were grown epitaxially under atmospheric pressure.

In Fig.2, the X-ray θ-ϕ pole figure with a 2θ fixed at the (111) reflection of the as-deposited quartz film is shown. It is seen that six poles separated by an angle of 60º, which is the evidence that the [001] axis is perpendicular to the film because the hexagonal crystal with the [001] orientation has sixfold symmetry. Also, it was found that the deposition of SiO_2 buffer layer of 50 nm at 500 ºC prior to the quartz deposition improves the quality of the deposited quartz films (Fig.2).

Consequently, it was confirmed that the Cat-VPE technique using gaseous HCl as a catalyst makes it possible to grow quartz thin films with hexagonal structure epitaxially at a low temperature of 570 ºC [1].

B. Growth of Quartz Thin Films with AT-Cut Surface

It has been well known that the AT-cut plates are used as an oscillator because their oscillation frequency is independent of temperature. However, one should remember that the AT-cut surface is not a particular lattice plane specified by (*h, k, l*) and its direction on the basis of the [001] and [011] directions are 35.25 and 2.96º apart, respectively. For this reason sapphire substrate with the $(11\bar{2}0)$ surface was used for the growth of quartz with AT-cut surface.

Two- and three step growth were examined for the AT-cut quartz film growth, whose processes involved single- or two-step SiO_2 buffer deposition at 500 ºC and 500 and 450 ºC, respectively, prior to the quartz film deposition at 570 ºC.

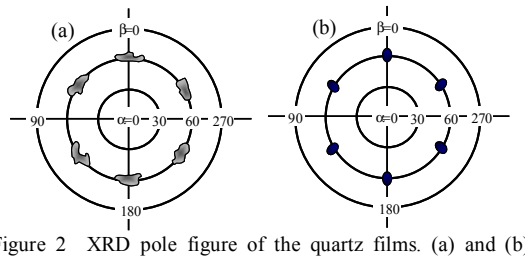

Figure 2 XRD pole figure of the quartz films. (a) and (b) denote the film with the SiO_2 buffer layer thickness of 0 and 50 nm, respectively.

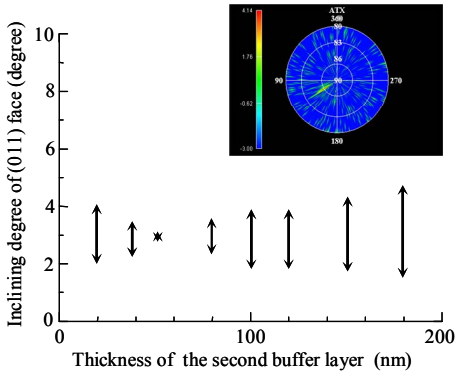

Figure 3 Effect of the second buffer on the angle of inclination of the quartz (011) face. Vertical arrow lines indicate the degree of the spreading spot centred around 3º, and the graphic chart in the figure is a typical X-ray pole figure of the as-deposited quartz film.

Other conditions were as follows: partial pressures of $Si(OC_2H_5)_4$, O_2 and gaseous HCl were 3.3 x 10^2, 3.3 x 10^4, 1.7 x 10^2 Pa, respectively. Total flow rate was 1.33 x 10^{-5} m^3 s^{-1}.

In the comparison of the XRD rocking curves at ω = 13.291º for quartz films prepared by two- and three-step growth, it was found that the latter films gave narrower line with a full width at half-maximum (FWHM) than the former ones. A best value of FWHM = 0.005º was obtained when the thickness of the first and second buffer layer was 100 and 50 nm, respectively, although a FWHM value of 0.05º was reported in our previous paper [3].

Fig.3 shows the X-ray pole figure of the as-deposited quartz film with a 2θ fixed at the (011) reflection of quartz, in which the centre of a circle corresponds to the $[1\bar{1}20]$ direction of the sapphire substrate. One should remember that if a spot appears at the centre, the (011) surface of the quartz grows perpendicular to the substrate surface. As is seen in Fig.3, a bright spot due to the reflection of the as-deposited quartz is observed at 3º off from the centre. This means that the [011] direction of the as-deposited quartz film is tilted 3º off from the normal to the sapphire $(11\bar{2}0)$ surface, indicating that the quartz film deposited grow with an approximate AT-cut surface. Also, it is worth noting that the bright spot was spread minimum when the thickness of the first and second buffer layer was 100 and 50 nm, respectively, in accordance with the results of the X-ray rocking curve measurements described above.

Raman spectroscopy was applied in order to elucidate the difference between two- and three-step growths. It was found that the first buffer layer gave a complicated spectra appearing broad bands centred at 1193 and 1064 cm^{-1} assigned to LO (O-Si-O anti-symmetric stretching) and TO (O-Si-O anti-symmetric stretching) modes, respectively, and 602, 490, and and 448 cm^{-1} assigned to 3-, 4- and multi-rings consisted with Si and O atoms. On the contrary, the surface after the second buffer deposition gave a simple spectral pattern with a strong narrow line at 465 cm^{-1} and a weak one at 206 cm^{-1} assigned to LO+TO modes, which is the same pattern as that of quartz. This implies that the second buffer plays a role in improving the quality of quartz film which grows on it.

By employing synchrotron radiation methods, quality of the as-deposited quartz films was examined. The luminescence excitation spectra, which are very sensitive to the quality of the material, are assessed for both band edge (excitonic) and core-level Si *L*-edge excitations. It was found that the optical and structural properties of the as-deposited quartz were the same as that prepared by hydrothermal method, verifying the high quality of the quartz grown by the catalyst-enhanced vapour phase epitaxy method [5].

Why does the quartz film of (011) surface grow tilted 3° off from the normal to the sapphire $(11\bar{2}0)$ surface? There is no means to investigate this phenomenon. It may be interpreted as follows: From the comparison of the packing diagrams of quartz and sapphire shown in Fig.4, it is seen that the hexagons consisting of Al in sapphire $(11\bar{2}0)$ and Si in quartz(011), which are marked by dashed line, have a least mismatch of 3 %, so that quartz would grow along with the direction. Taking it consideration of the fact that the quartz(011) surface grows 3° off from the sapphire $(11\bar{2}0)$ surface, it implies that the adjustment by an oxygen atom every four-quartz hexagons growth occurs.

IV. Conclusion

It was summarised a direct growth method of the quartz films by means of chemical vapour deposition which we studied. The most remarkable conclusion is the findings that the catalyst-enhanced vapour phase epitaxy makes it possible to grow the quartz films. A key to the success lies in gaseous HCl which plays a role in the catalyst which enable to low temperature decomposition of $Si(OC_2H_5)_4$ at 570°. Another point is that for the deposition onto sapphire $(11\bar{2}0)$ surface quartz(011) surface grows in the 3° off direction from the substrate surface.

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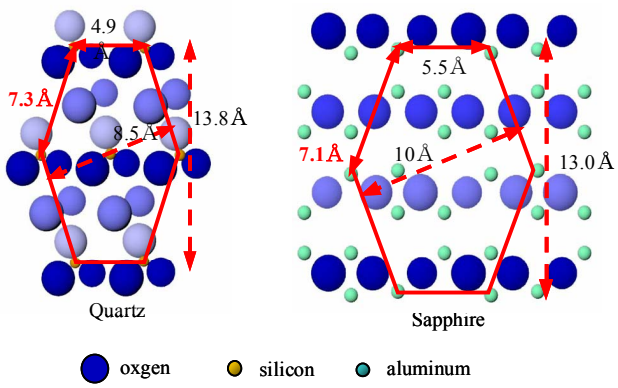

Figure 4 the packing diagram of quartz and sapphire projected perpendicular to the [011] and [110] axes, respectively

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