Fabrication of Magnetolectric Cr$_2$O$_3$ Films for Application
Single Flux Quantum Device

Takeshi Asada, Kenjirou Nagase, Takayuki Yamada, Nobuyuki Iwata and Hiroshi Yamamoto
College of Science & Technology Nihon University (CST), 7-24-1 Narashinodai, Funabashi-shi, Chiba 274-8501
Fax: +81-47-469-5457, e-mail: 2003_asada@vamanova.ees.nist.nihon-u.ac.jp

Thin films of magnetolectric (ME) materials are expected to be applied to novel superconducting devices as voltage-controlled magnetic/current sources and gates. As a representative ME material Cr$_2$O$_3$ films were prepared on R-cut sapphire substrates by DC-RF hybrid magnetron sputtering. Strong Bragg diffraction peaks (n 0 - n 2n) from Cr$_2$O$_3$ with a trigonal phase were observed. Then full width at half maximum of rocking curves of (10-12) was 0.58 degrees in the film deposited on substrate of 500°C substrates. The surface morphology of the film prepared at 550°C was very smooth with a step and terrace structure. The steps height was same the lattice spacing of Cr$_2$O$_3$ (10-12) planes. The Cr$_2$O$_3$ films deposited on Nb-SrTiO$_3$ (100) with CeO$_2$ buffer layers revealed c-axis or c-axis oriented growth. The CeO$_2$ buffer layer proceeded the growth of Cr$_2$O$_3$. A leakage current through the Cr$_2$O$_3$ film was suppressed less than $10^{-5}$ A/cm$^2$ below the electric field of 0.24 MV/cm.

Key words: magnetoelectric effect, Cr$_2$O$_3$, Nb-STO, CeO$_2$ buffer, epitaxial growth

1. INTRODUCTION
A magneto-electric effect is defined as an appearance of magnetic fields induced by electric fields. When electric fields are applied, the deviation of ± ions in the crystal takes place and results in changes of magnetic superexchange interactions and magnetic fields appear outside [1,2]. As a representative ME material antiferromagnetic insulator Cr$_2$O$_3$ has been studied [3]. Since magnetic fields are induced along the direction of electric fields applied, the orientation and crystallinity of the ME material are determining factors. It is expected that thin films of ME materials are applied to novel superconducting Josephson devices with voltage-control type of magnetic or current sources and gates. Fig. 1. shows the schematic example of a single flux quantum (SFQ) device fabricated by both cuprate high temperature superconductors (HTS) and ME thin films. When electric fields are applied to the ME thin film, magnetic fields are induced to generate shielding current in the superconductor loop including Josephson junctions. The novel circuit element enables a dispersed current source system for highly integrated SFQ circuits and also improves the performance of 100GHz class of high speed SFQ switching.

Most of HTS circuits have been prepared on cubic perovskite substrates, SrTiO$_3$ (STO) or MgO. A crystal matching is not good between the substrate crystal and the trigonal Cr$_2$O$_3$. Cr$_2$O$_3$ films should be deposited on STO substrates buffered by cubic CeO$_2$ which has been studied for preparation of HTS thin films [4-7]. The purposes of this work are to optimize the substrate temperature for sputtered Cr$_2$O$_3$ films on R-cut sapphire (10-12) and to investigate the film growth on Nb-SrTiO$_3$ (STO) with CeO$_2$ buffer layers.

2. EXPERIMENTAL
Cr$_2$O$_3$ films were deposited by off-axis DC-RF hybrid magnetron sputtering from a Cr metal target with the diameter of two-inch [8]. The typical growth conditions were as follow: substrate temperature (T$_s$) of 300~600°C, DC current of 0.04 A, RF power of 100 W and sputtering pressure of 0.26 Pa (Ar:O$_2$:4:1). Substrates of R-cut sapphire single crystals (5 x 10mm$^2$) were etched by HF(HF:H$_2$O=1:7) for 10 s before annealing at 1000°C for 12 hour in the air. As a substrate, CeO$_2$ buffer layer was deposited by off-axis RF magnetron sputtering on Nb-STO(Nb 0.5w% dope) and post-annealed at 500 or 1000°C in the air. Several CeO$_2$/Nb-STO substrates with different average roughness (Ra) were obtained and compared with the results for the Cr$_2$O$_3$ films growth.

The crystalline structure of the films was analyzed by X-ray diffraction (XRD: Rigaku RAD-C) with 2θ-θ scan from 5 to 90 degrees. Surface morphology was observed by an atomic force microscopy (AFM: Seiko Instruments Inc. Nanonavi-station).
3. RESULTS & DISCUSSION

3.1 Growth of Cr$_2$O$_3$ thin film on the R-cut sapphire

Fig. 2. shows the XRD pattern of Cr$_2$O$_3$/R-cut sapphire prepared at $Ts=500^\circ$C. The open-circles peaks show the peaks from the sapphire substrate. All Bragg diffraction peaks were assigned to R-plane (n 0 n 2n) of trigonal Cr$_2$O$_3$ phase and the substrate. The lattice spacing evaluated from the Cr$_2$O$_3$ (10-12) peak was 0.363 nm same to that of bulk crystal. Fig. 3. shows the enlarged (10-12) peaks of the films deposited at $Ts=500\sim600^\circ$C. Crystallization of the trigonal Cr$_2$O$_3$ phase was confirmed at $Ts$’s above $300^\circ$C.

Fig. 4. shows the full width at half maximum (FWHM) of Cr$_2$O$_3$ (10-12) rocking curve. The smallest FWHM was 0.58 degrees in the film prepared at $Ts=500^\circ$C, which revealed the superior crystal growth.

Since the inplane lattice parameter of R-planes of Cr$_2$O$_3$ is larger by about 4% than that of R-cut sapphire. The lattice spacing of Cr$_2$O$_3$ films are contracted in planes by internal compressive stress and are expanded perpendicular to substrate planes by tensile stress.

From the results of XRD it was found that the lattice spacing of the film at $Ts=500^\circ$C. was almost same to that of the bulk and the internal stress was relieved.

Fig. 5. shows AFM surface images and line-profiles of Cr$_2$O$_3$ films prepared at various $Ts$’s. In (a-1) at

![AFM surface images and line-profiles of Cr$_2$O$_3$ thin films prepared at various $Ts$’s.](image-url)
Ts=400°C, characteristic rectangle grains appeared with the size 100×100–200nm². From the line-profile (a-2), the average bump between grains was approximately 3.5nm. The average roughness (Ra) was comparatively small, 1.5nm. In (b-1) at Ts=500°C, the grains coalesced and their shape changed into square. In (c-1) at Ts=550°C, the coalescence proceeded more clearly and grain boundaries decreased. As shown in the focused line-profile (c-3) several steps were clearly observed in one grain plane. Those steps height was same the lattice spacing of Cr₂O₃ with R-plane (0.363nm). The surface morphology suggested the 2-dimensional growth took place on 550°C substrates. In (d-1) at Ts= 600°C, the grain size became larger. The bump of grains increased as increasing Ts. The value of Ra was large, 4.2nm and bunching steps increased. A step and terrace structure disappeared as shown in (d-2).

It is thought that the grain boundary is caused by the internal stress which is induced from the lattice mismatch. As stated in the XRD result the inplane stress from the R-cut sapphire was relieved at about 500°C. The surface of the film prepared at the 550°C was very smooth and revealed 2-dimensional growth. Conclusively the results of XRD and AFM suggested that the growth of Cr₂O₃ is superior at Ts=500–550°C and results in an excellent step and terrace structure which suggests the possibility of an epitaxial growth.

3.2 Growth of Cr₂O₃ on the Nb-STO with CeO₂ buffer

Cr₂O₃ films were not grown directly on the STO substrate. Then the buffer layers of CeO₂ were prepared. Fig. 6. shows XRD patterns of Cr₂O₃/CeO₂/Nb-STO bi-layers (sample A, B and C). The sample A was deposited on the rough CeO₂ layer which was not post-annealed after sputter deposition and has Ra=4.2nm. No Bragg diffraction peak from Cr₂O₃ was observed. The sample B was prepared on the smooth CeO₂ @Ra=0.41nm layer, post-annealed at 1000°C. The sample revealed a c-axis oriented growth of the trigonal Cr₂O₃. The sample C was deposited on the CeO₂ layer post-annealed at 500°C and showed mixed phase growth with a-axis orientation. The Cr₂O₃ (n n -2n 0) and (30-30) peaks were observed. The results of XRD indicated that the trigonal Cr₂O₃ grew on the CeO₂ (100)/STO(100) with a-axis or c-axis orientation.

The AFM surface images of sample A and B were shown in Figures 7(a-1) and (b-1). Figures 7(a-2) and (b-2) show the surface morphology of the CeO₂ (100) substrate for sample A and B, respectively. In the film (a-1) grown on the substrate (b-1) various sizes of grains and deep valleys of grain boundaries were observed. The depth of the valley was above 70nm and the value of Ra was ca. 17nm. In the film (b-1) on the substrate (b-2) smooth surfaces with Ra of 4.2nm were observed.

The surfaces of sample A were not smooth and no Bragg diffraction peak was observed. On the other hand, hexagonal grains appeared in smooth surfaces of sample B. So it was thought that the smooth part of sample B corresponded to c-planes of Cr₂O₃. These results suggested that the smoothness of the CeO₂ layer affected to Cr₂O₃ growth as a dominant factor and applications of Cr₂O₃ films are fulfilled for SFQ electronic devices fabricated on STO substrates.

Fig. 8. shows a leakage current density as a function of applied electric field in sample B. The diameter of the measuring electrode was 0.45mm and the total thickness of the Cr₂O₃/CeO₂ film was ca. 230nm. The observed leakages current was suppressed less than 10⁻⁶A/cm² below electric field of 0.24MV/cm, the applied voltage of about 5V. So the Cr₂O₃ film works as the ME material under the order of 0.1MV/cm.

Assuming that the ME coefficient of Cr₂O₃ along the
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\( c \)-axis is \( 10^4 \) at about 50K [9, 10], the expected magnetic field in the film is about 1 Gauss. Also the magnetic field induced at 300K attains up to 10 Gauss, ten times as large as that at 50K.

![Figure 8](image_url)

Fig. 8. The leakage current density vs. applied electric field in sample B of \( \text{Cr}_2\text{O}_3/\text{CeO}_2/\text{Nb-STO} \). The bi-layered film was an insulator below electric field of ca. 0.24 MV/cm.

4. CONCLUSION

The ME \( \text{Cr}_2\text{O}_3 \) films were prepared on the \( R \)-cut sapphire and on Nb-STO with \( \text{CeO}_2 \) buffers by sputtering. The 2-dimensional growth of \( \text{Cr}_2\text{O}_3 \) was observed on the \( R \)-cut sapphire at \( 500\sim550 \)°C. The \( \text{CeO}_2/\text{Nb-STO} \) substrate successfully resulted in the growth of \( \text{Cr}_2\text{O}_3 \) with \( c \)-axis and \( c \)-axis orientation. The prepared \( \text{Cr}_2\text{O}_3/\text{CeO}_2/\text{Nb-STO} \) revealed the superior insulating properties and assured comparatively large magnetic field of about 1 Gauss. The obtained results strongly suggested that the \( \text{Cr}_2\text{O}_3 \) films are applicable for novel SFQ devices fabricated on cubic STO substrates.

5. REFERENCES


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