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HRTEM and STEM observation for surface atomic structures of $SrTiO_3$ substrate

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SrTiO3 single crystals are widely used as substrates for the epitaxial growth of perovskite oxide thin films. To obtain high quality film, it is necessary to control surface structures of the substrates at an atomic scale. For this purpose, it is known that annealing the surface in air or in ultra high vacuum is quite effective to form step structures on (100) surface of $SrTiO_3$. So far, many studies have been reported for the step structures concerned with the surface termination layer, particles and surface reconstructions[1-2]. In these studies, it has been revealed that atomic structure on $SrTiO_3$ (100) surface greatly changes against annealing conditions such as temperature, time, and oxygen partial pressure, however, there are few reports about the dopant effects. In this study, we examined the dopant effects on the formation of surface structure in $SrTiO_3$ (100) surface by HRTEM and STEM.

Commercially available undoped and 1wt% Nb-doped $SrTiO_3$ single-crystals with (100) orientation (Furuuchi Chemical Co.,Ltd., Japan) were used in this study. HRTEM and STEM-HAADF observations were carried out for a plan view and a cross sectional view of the surfaces. Plan-view thin foils were prepared by conventional back thinning methods including mechanical grinding and dimpling. After ion thinning, the thin foils were annealed in air or in reducing atmosphere using 95%Ar +5%H_2. Thin foils for cross sectional observation were prepared by joining the annealed substrates in face-to-face with glue. After that, the joint samples were mechanically ground, polished and ion-milled.

Figure 1 shows a plan view HRTEM image of undoped $SrTiO_3$ (100) sample annealed at 1000℃ for 2h in air. The line contrasts on the surface are traces of the steps formed on the surface by annealing at elevated temperature. As indicated by arrows in the image, all of the traces are parallel to [010] or [001] direction as confirmed by the diffraction pattern. Surface step structures sometimes exhibits wavy features, i.e., in AFM image and so on. However, all the steps consist of fine segments parallel to [010] or [001] at an atomic scale even in such wavy traces.

Figure 2 shows HRTEM image taken from an edge area of the annealed substrate. Distinct features can be seen in the image. Two different planes appear at the edge area, whose traces are parallel to [110] and [001]. After long time annealing, the area parallel to [001] was confirmed to increase, however, [110] edges always remain in spite that such area becomes smaller. For example, the area can be seen at a corner of the two [001] areas. With this fact, (011) habit is also stable one at this annealing temperature in addition with (001) habit.

Figure 3 shows STEM-HAADF image taken from undoped $SrTiO_3$ (100) substrate prepared by similar condition of the substrate in the Fig. 1. In the image, two contrasts can be seen, i.e., brighter spots correspond to Sr columns and the others to Ti-O columns. With this method, we can directly know the atomic column positions. The inset in the image is an intensity profile obtained from a square region as shown in the image. The terminated columns as indicated by the arrows are Ti-O columns as recognized with the image and also the intensity profile. Namely, in the annealing condition used in this study, surface terminated atomic layer is TiO_2 planes.

The formation of this structure can be discussed in terms of the vacancy formation energy. Tanaka *et al*. have carried out theoretical calculation for vacancy formation energies, ΔH, in $SrTiO_3$ [3]. According to their results, ΔH of Sr vacancy is lowest at the condition of annealing used in this study. By annealing at oxidizing atmosphere, Sr vacancies tend to generate more comparing Ti vacancies near the surfaces. The imbalance formation of the vacancies possibly determines the terminated layers. In addition, a very thin region, which includes many Sr vacancies, has been confirmed to form near the surfaces by EDS and

EELS. With this concept of control of vacancy formation energy, we can control the surface atomic layers by changing a kind of dopants. In the presentation, the results of doped $SrTiO_3$ will be shown.

Acknowledgement

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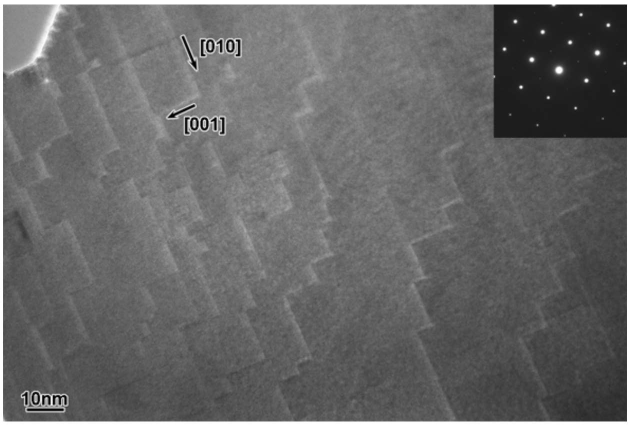

Figure 1
HRTEM plan view image of (100) $SrTiO_3$ substrate annealed at 1000℃ for 2h in air.

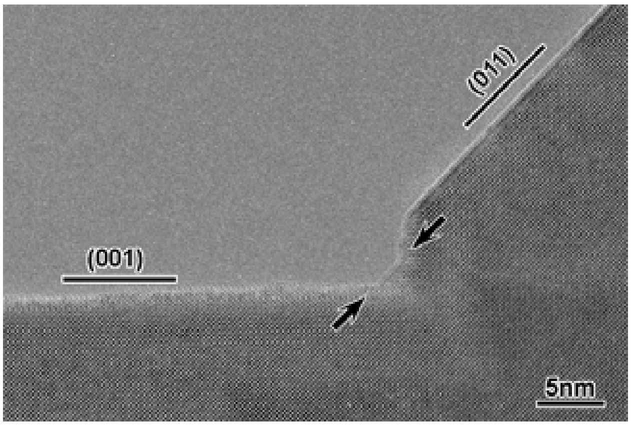

Figure 2
A magnified HRTEM image near the edge region as shown in Fig. 1.

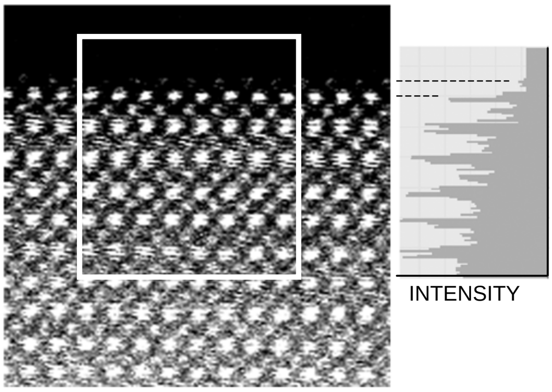

Figure 3
STEM-HAADF image of (100) $SrTiO_3$ substrate annealed at 1000℃ for 2h in air. The inset is an intensity profile taken from a square region in the image.