NW10A/2013G551

Local structure of Nb in a TiO_2 rutile single crystal

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1 Introduction

TiO_2 is a n-type oxide semiconductor which has a high conductivity by doping of impurity, oxygen vacancy and interstitial metal. Nb is one of the typical dopants. Sasahara recently reported that Nb was present in the interstitial position on the surface as Nb^{5+} [1]. Zimmerman interprets the ESR signals using the Nb^{4+} substitution on the Ti^{4+} site and hopping conductivity.[2] In this work we applied Nb K-edge EXAFS to identify the location and the valence state of Nb in the bulk.

2 Experiment

The Nb doped TiO_2 rutile single crystal was purchased from Shinko-sha(0.05wt%; 5Ωcm). EXAFS spectra were measured using a Si(311) double crystal monochromator at NW10A of Photon Factory Advanced Ring(PF-AR). The fluorescence EXAFS was measured using 19 elements SSD. The [001] direction of the single crystal was oriented vertically with its surface normal directed to the 45 degree against the X-ray propagation direction. Thus the structure information in the (001) plane was mainly obtained. All measurements were carried out at room temperature.

3 Results and Discussion

Figure 1 shows the X-ray absorption near edge structure(XANES) of Nb in the TiO_2 single crystal. The XANES is quite similar to TiO_2(110) rutile with the polarization perpendicular to the c axis though the peak D was weaker than that of TiO_2.[3] The edge position appeared below that of the Nb_2O_5 and was close to that of the Nb_2O_3, indicating the presence of less than 5 + species, maybe Nb^{4+}.

Figure 2 shows the Fourier transform of Nb K-edge EXAFS. Two peaks appear; the first peak corresponds to the Nb-O and the second one to the Nb-Ti. Table 1 shows the curve fitting results. Nb-O and Nb-Ti distances were corresponding to those expected in the substituted Nb at the Ti site of the rutile when the polarized EXAFS was measured in the direction perpendicular to the c axis. Thus the Nb is located at the Ti position. If the Nb were present in the interstitial site there should be closer Nb-Ti interaction at less than 2.5 Å. The XAFS results did not support the interstitial location of Nb..

4 Conclusions.

We carried out the XAFS measurement of Nb in the rutileTiO_2 single crystal. Nb was located at the Ti position in the state of Nb^{4+}.

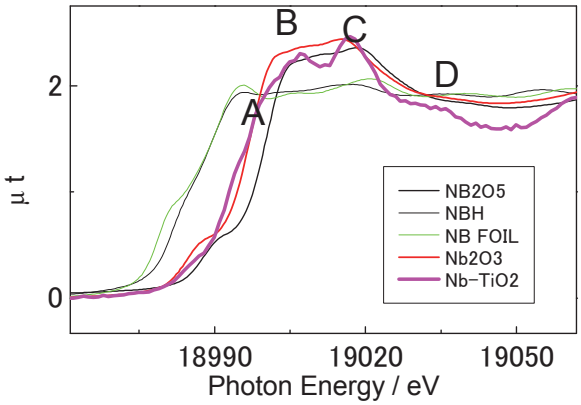

Figure 1 XANES spectra of Nb in TiO_2 together with reference compounds.

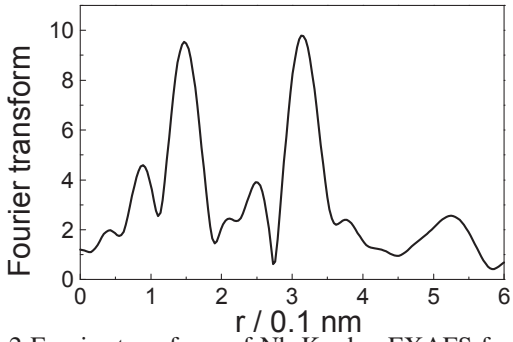

Figure 2 Fourier transform of Nb K-edge EXAFS for Nb in TiO_2.

Table 1 Curve fitting results of Nb EXAFS

	N	R/nm	σ	R/%
Nb-O	6(1)	0.198(2)	0.008(2)	7.7
Nb-Ti	7.5(1)	0.365(2)	0.004(1)	

References

[1] A. Sasahara and M. Tomitori, *J.Phys. Chem. C*, **117**, 17680(2013).
[2] P. H. Zimmermann, *Phys.Rev.B* **8**, 3917 (1973).
[3] Y. Joly, D. Cabaret, H. Renevier and C. R. Natoli, *Phys. Rev. Lett.* **82**, 2398 (1999).