Atomic Beam Detection with the Use of Single Crystal Surfaces of Transition Metal Mono-oxides

Y.FUJIMORI *and S.USAMI

**Laboratory of Applied Physics, Faculty of Engineering,*
Yokohama National University,
79-5 Tokiwadai,Hodogaya-ku,Yokohama 240-0067, Japan

Kanagawa Institute of Technology,
1030 Shimo-Ogino, Atsugi-shi,Kanagawa-ken 243-0203, Japan

Abstract

It was previously reported that the sintered transition metal oxides of the Ni-Mn-Co system could be used to detect atomic species of such common gases as hydrogen, deuterium, oxygen and nitrogen . The sensitivity for atomic beams correlates with the electrical resistivity of oxides, and its temperature dependence [Appl.Surf. Sci. 70/71(1993)351].

For the purpose of improving sensitivity for the atomic beam detection as well as getting more information on the reaction process of atomic beam with these surfaces, it was attempted to grow monocrystalline cobalt mono-oxides by the flame fusion technique and to examine their sensitivities.

CoO single crystal surfaces showed 10^3 times higher sensitivity than sintered polycrystalline surfaces.

Keywords: atomic beam, cobalt mono-oxide, nickel oxide, single crystal

1. Introduction

The dissociated species of gaseous molecules generally are highly reactive to surface layer atoms of condensed materials and can be used to modify the surface properties in electronic devices. It is important to study such interactions in detail with well-defined atomic beams to establish the basis of the irradiation technology of reactive atomic beams which can be applied in a wide scientific and technological area. Since the detection technique has not been well worked out, further studies on sensing atomic species are of great importance.

There are several techniques for selectively sensing atomic species, which are usually mixed together with non-dissociated mother gases. First, MoO_3 is a simple sensing material as it changes its colour from light yellow to blue when being irradiated with atomic hydrogen[8] . Next, ZnO[9] and Si[10] were used by measuring the change of their electrical resistance due to the adsorption of atomic species. ZnO shows a decrease of the resistance, while Si shows an increase. Both materials have to be heated intermittentely during the experiment because they lose the sensitivity due to saturation of adsorbates. This kind of detector may be called of accumulation type or of adsorption type. Transition metal oxides show the resistance change in the same manner, but in this case, no saturation is observed in its output signal. Such a feature is preferable as one can carry on the experiment without any intermission for necessary thermal treatment to regain sensitivity. So far, only polycrystal surfaces were used as an detector of atomic species. However, electrically high resistive materials such as single crystals are expected to have higher sensitivity.

In this paper, the sample preparation including the growth procedure of CoO single crystals with the flame fusion method was first described. Then, irradiation experiments of atomic species of hydrogen, deuterium, oxygen and nitrogen onto specimens were reported in detail. The sensitivity of CoO single crystal surfaces to the atomic species of common gas molecules was compared with

those of sintered polycrystalline CoO specimens.

2. Sample preparation

2.1. Growing single crystals of CoO

There are widely used various techniques for growing single crystals of transition metal oxides, such as flame fusion method (Berneuil method), chemical vapor deposition, Bridgman method, and flux method. Here, the flame fusion technique was used, as it needs no crucible for holding raw materials molten in a high temperature and one can grow a large size of crystals. In this method the control of gas flow is essential to grow crystals in stoichiometry. A coaxial three-tube burner was set up to supply hydrogen and oxygen gases for steady burning to melt powders of CoO. The raw material of CoO was 99.9% pure powder of less than 8 μ m of the particle size which was supplied from the Rare Metallic Co.

When growing a crystal, it is important to fall down the raw material of CoO powder upon a growing seed at a constant rate. The reservoir from which the CoO powder falls down through a #150 mesh, was tapped by a hammer 10 times per minute. The flow of hydrogen gases as a burning fuel in an outer tube and that of oxygen gases in an inner tube were controlled at the flow rate of 12.25 l/min. and 9.5 l/min. respectively using gas flow meters. Under this condition, CoO crystals of 10 mm in diameter and 20mm in length were grown in 3.5 hours. Thus obtained crystals were annealed at 900 ~ 1000° C in a furnace for a week at the atmospheric pressure in order to remove an excess of oxygen [5][6].

2.2. Preparation of specimens

The crystal structure of CoO is of NaCl type, and the low index planes (100), (110) and (111) of the crystal have two dimensional different configurations from each other. Therefore, to examine the surface structure dependence of the sensitivity, low index crystal surfaces were prepared in the following manner. The (100) surface plane is readily prepared by cleavage along a (100) plane of crystal , however, (110) and (111) planes were prepared by cutting bulk crystals using a wire saw in a desired direction after being determined with the Laue X-ray diffraction.

After mechanical polishing in a mirror finish, specimens were formed in a thin rectangular plate of 2×5 mm, 1mm in thickness and Au lead wires of 0.2 mm in diameter were connnected to both edges of the longer side using silver paste followed by heat treatment at 130° C for 1.5 hours.

3. Experimental

In a vacuum chamber of 10^{-7} Pa, specimens were mounted on a manipulator which had a facility to control the temperature of specimens in a wide range from the liquid nitrogen temperature to 300° C.

The equipment for the atomic beam source was reported in a previous paper[1]. Briefly, molecular gases at a low pressure of 40 Pa were discharged with an r.f. power source of 100W at 2450 MHz.

The detection of atomic beam was performed by measuring the change of the electrical resistivity of specimen which was induced by irradiation of an atomic beam. The resistance change

was observed with a bridge circuit, together with a lock-in amplifier to detect the unbalanced output of the bridge.

The typical intensity of atomic hydrogen beam was estimated to be 10^{13} atoms per cm^2 with the assumption that the dissociation rate of hydrogen was 60% under the gas pressure of 40 Pa [7]. Here in this study, it was not attempted to determine absolute sensitivity because of no reliable values obtained for gas dissociation rates. However, since the working conditon of the atomic beam source was kept unchanged, the relative sensitivity between different kinds of atom and also between different surfaces of a specimen are not meaningless.

4. Results and discussion

The resistivity of specimens were too high to measure at room temperature, so that the temperature of the specimens was raised at 373 K. The resistivity changes due to atomic beam irradiation were observed by repeating discharge on and off (the irradiation of atomic beam is on and off). Figure 1 shows the ratio of the resistance change ΔR to the whole resistance R of CoO(100) as a function of irradiation time for atomic hydrogen, oxygen, nitrogen and deuterium.

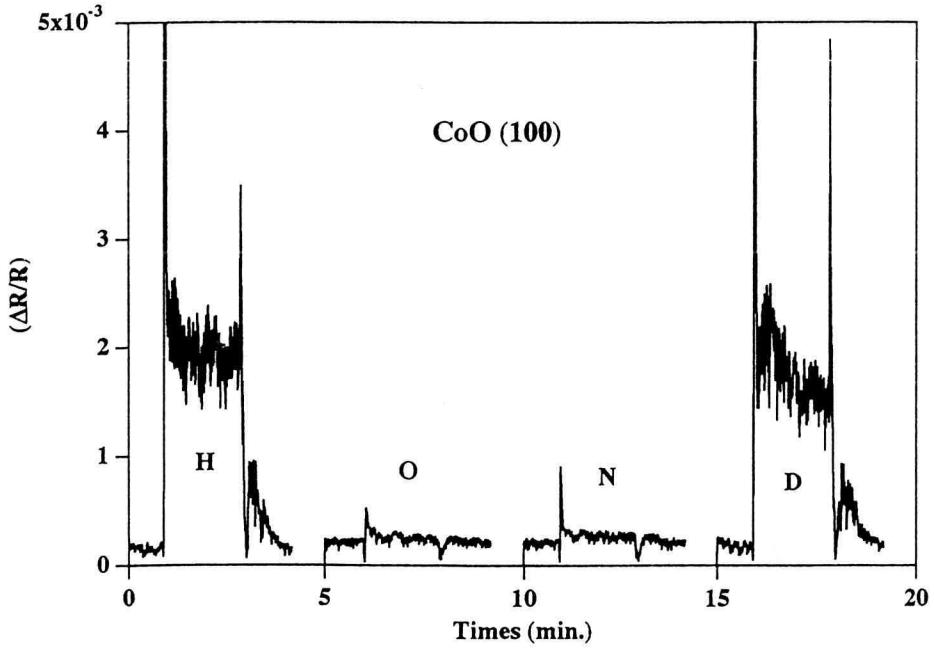

Fig.1. The relative resistance change $\Delta R/R$ of CoO(100) vs. irradiation time of atomic species.

Figures 2 and 3 show $\Delta R/R$ for CoO(110) and CoO(111) measured in the same manner. In comparison, $\Delta R/R$ for NiO(100) is also shown in Fig.4. All results are summarized in Table 1, where the results of some sintered oxides were cited from the reference [1] to compare with.

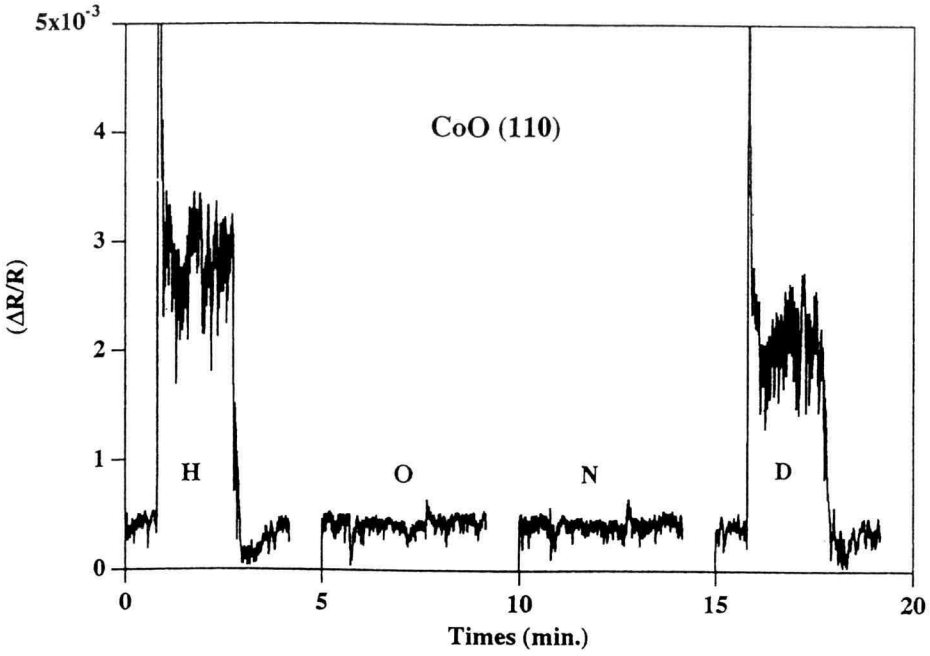

Fig.2. $\Delta R/R$ of CoO(110) vs. irradiation time of atomic species.

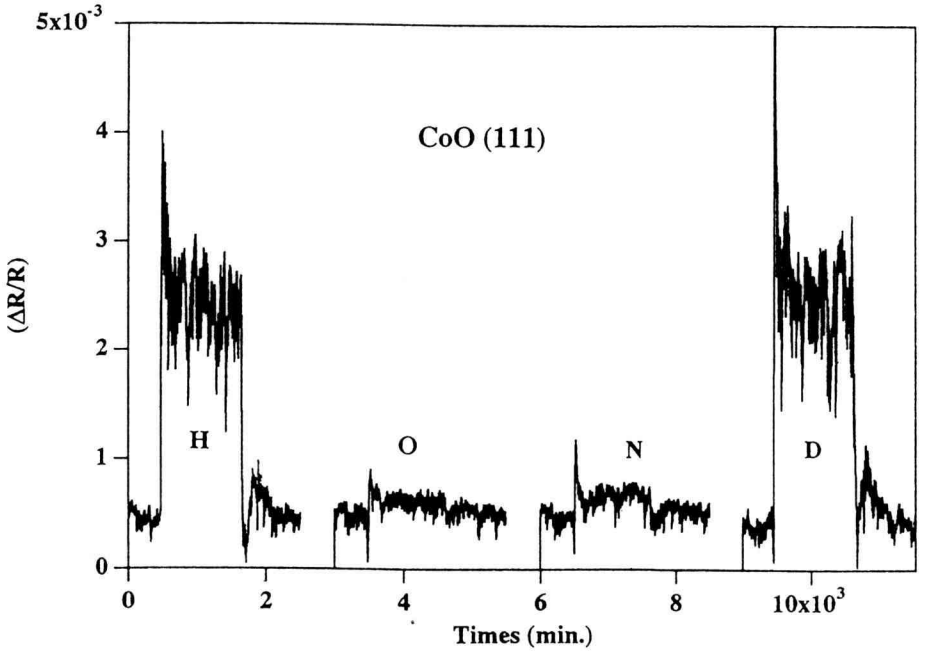

Fig.3. $\Delta R/R$ of CoO(111) vs. irradiation time of atomic species.

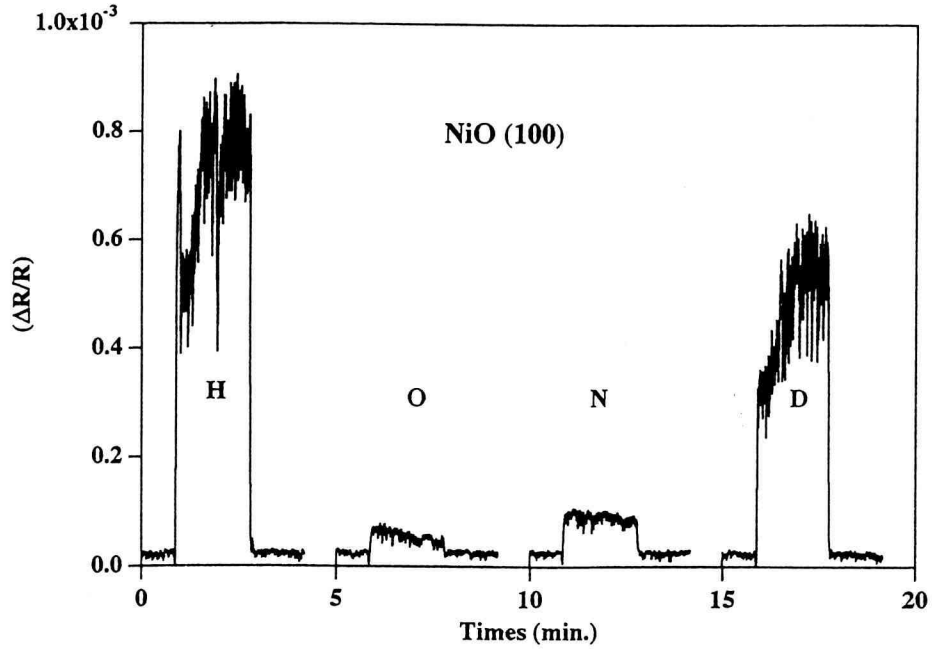

Fig.4. $\Delta R/R$ of NiO(100) vs. irradiation time of atomic species.

Table I. The summerized results for single crystals and sintered materials. The electric resistance was measured at the pressure of about 10^{-7} Pa. Here, the sensitivity (Sens.) is expressed with $\Delta R/R$.

Specimen	CoO (100)	CoO (110)	CoO (111)	Sintered cobalt oxide[1)]	NiO (100)	Sintered nickel oxide[1)]
Temp. (K)	373	373	373	273	373	273
Resist. (Ω)	820 M	720 M	1.40G	311.9 K	4.22 M	230.6 M
Chop. (Hz)	10	10	10	80	10	80
Factor				× 4		× 4
Sens. (H)	2.2×10^{-3}	1.8×10^{-3}	2.0×10^{-3}	8.9×10^{-6}	6.5×10^{-4}	2.9×10^{-4}
Sens. (D)	1.7×10^{-3}	1.6×10^{-3}	2.1×10^{-3}	9.1×10^{-6}	4.4×10^{-4}	3.0×10^{-4}
Sens. (N)	———	2.9×10^{-5}	2.5×10^{-4}	———	6.3×10^{-5}	7.8×10^{-5}
Sens. (O)	———	6.3×10^{-5}	1.7×10^{-4}	———	3.8×10^{-5}	3.9×10^{-5}

As seen in Table I, all low index crystal planes of CoO indicated 10^3 times larger $\Delta R/R$ than that of sintered cobalt oxide. The single crystal surface of NiO(100), however, showed a similar result to that of sintered NiO.

In earlier, Harvey and Fehrenbach examined to detect atomic hydrogen with a commercial thermistor which was a sintered mixture of nickel, manganese and cobalt oxides[2]. They observed the sensitive properties of the above material and interpreted the kinetics in term of the physisorption process as follows. A physisorbed adatom on the surface of the oxide immediately desorbs when it is recombined with another adatom to form a molecule, suggesting no accumulation of adatoms on the surface that results in no saturation effects. This is consistent with the experimental results shown in the above figures.

Harvey et al. further proposed the possibility of cooperation of chemisorption process. Chemically adsorbed atoms generally are bound strongly to surface atoms so that such adatoms can not be removed from the surface unless being heated at high temperatures. However, they assume that grain boundaries in a sintered oxide could give rise to open routes for the desorption of adsorbates. The measurement in this work showed that the surface of single crystals which is expected to have no grain boundaries and low density of defects has much higher sensitivity than those of sintered oxides. This suggests that the chemisorption process would be not the case for the interaction between the atomic beam and the surface of transition metal oxide.

5. Summmary

The low index single crystal surfaces of CoO (100), (110) and (111) showed much higher sensitivity than polycrystalline surfaces of CoO by a factor of 10^3, suggesting that it is possible to detect atomic beams of much lower intensity .

The detection kinetics would be attributed to physisorption which is followed by the recombination of adsorbates as a molecule, leaving the exothermal energy to the surface. Even if the chemisorbed species would be present, they could be scarcely desorbed because of much less grain boundaries at a single crystal surface. Since no saturation was observed, the latter should be only a minor contribution in the whole process.

Appendix

The cobalt oxide is one of antiferromagnetic materials and its curie point is close to a room temperature. It interested the authors to measure the magnetic properties of prepared crystalline CoO to check its quality. Figure 5 and 6 show magnetization curves for CoO(111) at room temperature and at liquid nitrogen temperature respectively. Figure 7 shows the temperature dependence of magnetization for CoO(111). The Néel temperature was found at 295 $\pm$5 K which is in good agreement with the reported value of 293 K[11].

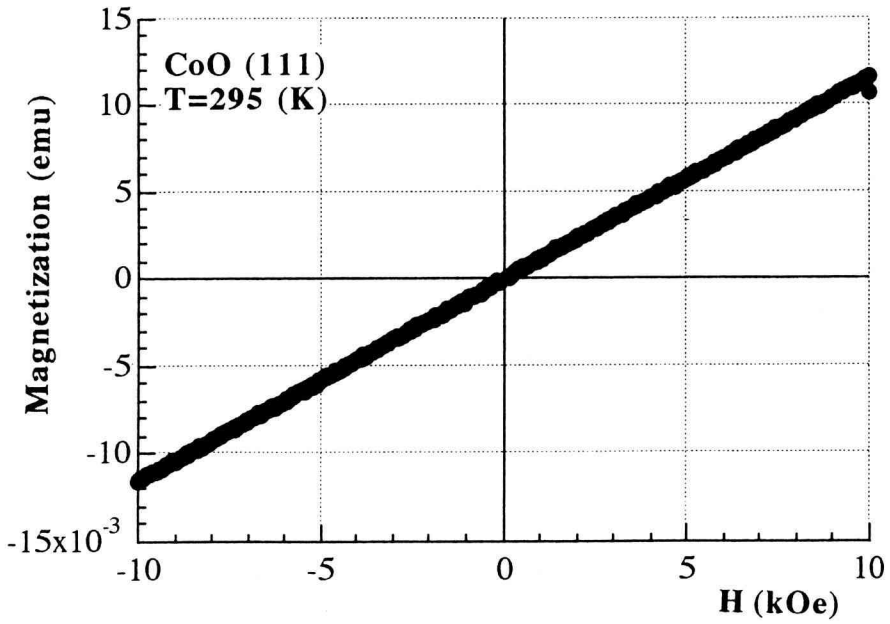

Fig.5. Magnetization of the prepared CoO (111) at room temperature.

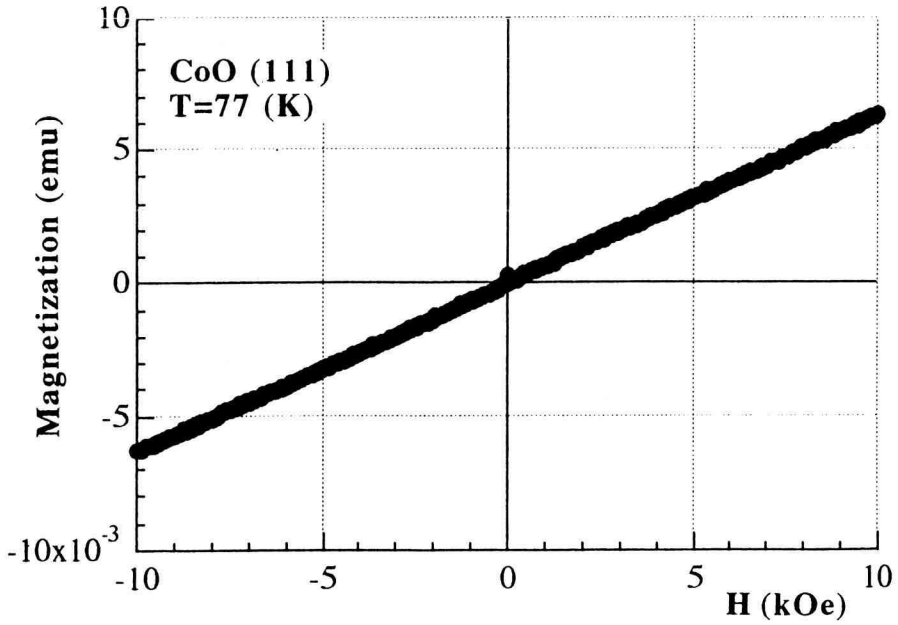

Fig.6. Magnetization of the prepared CoO (111) at liquid nitrogen temperature.

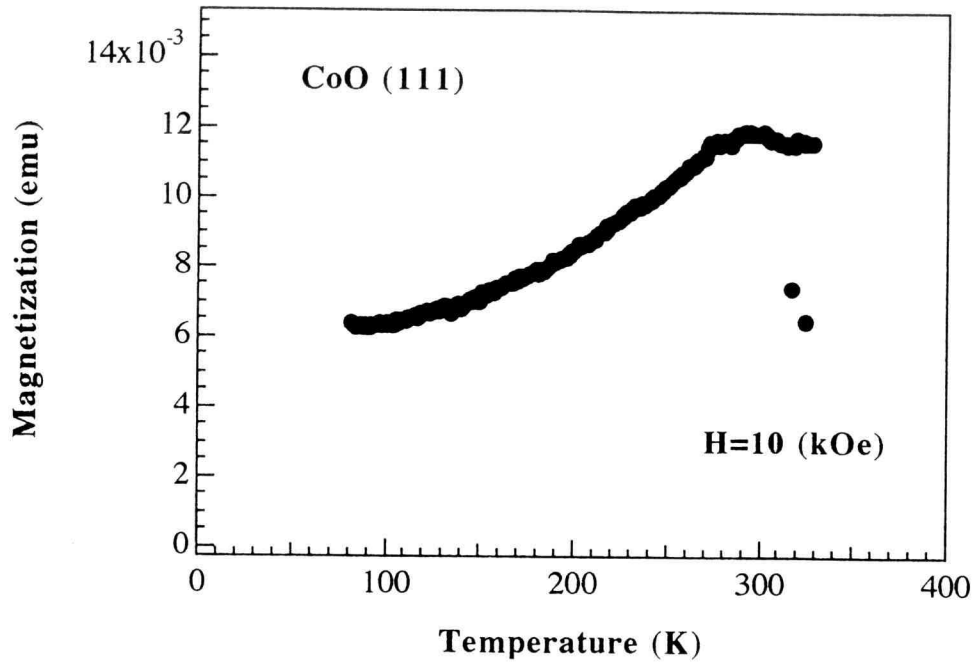

Fig.7. Temperature dependence of magnetization of the prepared CoO (111) under the magnetic field of 10 kOe.

Acknowledgements

The authors wish to thank to Mr.K.Ihara and Mr. T.Endo for their cooperation in growing crystals, to Mr.Y.Shimada for the measurement by EPMA, to Dr.I.Umehara, Dr.Y.Adachi and Prof. K.Sato for measuring X-ray diffraction and magnetization (Yokohama National University). We are also gratefulal to Mr.T.Yonezawa (Shinkosha Co.) for his technical advice on applying the flame fusion method, to Mr.K.Yamada (Sanley reinetsu Co.) for his advice on safety about three-tube burner, to Dr. K. Fukutani and Prof.Y. Murata (the Institute for Solid State Physics, the University of Tokyo) for their assistance in specimen preparation and Emeritus Prof.N. Miyata for his encouragement. This work was partly supported by a Grant-in-Aid for Fusion Research under the Special Research Project on Nuclear Fusion.

References

[1] Y. Fujimori, S. Kume and S. Usami, Appl. Surf. Sci. 70/71(1993)351.
[2] K.C. Harvey and C. Fehrenbach, Jr., Rev. Sci. Instr. 54(1983)1117.
[3] Y. Fujimori, Doctoral Thesis
(Yokohama National University, Faculty of Engineering, 1995).
[4] L. Merker, J. Amer. Ceram. Soc. 45(1962)366.
[5] E. Aukrust and A. Muan, Trans. AIME 230(1964)379.
[6] G.P. Sykora and T.O. Mason, Advances in Ceramics 23(1987)45.
[7] A. Ding, J. Karlau and J. Weise, Rev. Sci. Instrum.48(1977)1002.
[8] J.C. Macfarlane, J. Vac. Sci. Technol. 5(1968)118.
[9] K. Haberrecker, E. Mollwo, H. Schreiber, H. Hoinkes, H. Nahr and H. Wilsch,
Nucl. Instr. Methods 57(1967)22.
[10] A. Jacob, J. Appl. Phys. 46(1975)5116.
[11] La Blanchetais, J. de Phys. Rad. 12(1951)765.