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Analysis of hydrogen in Nb thin films and Nb/Cu multilayers, using ion beams

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Abstract

A Nb/Cu multilayered structure was prepared on sapphire substrate using molecular beam deposition technique. The prepared structure and the hydrogen incorporation behaviors were examined using 16 MeV $^{16}O^{5+}$ RBS before H-charging and ^{15}N-NRA after H-charging. Both the Nb and Cu layers are found to be strongly textured, through planar channeling experiments, with the same crystallographic symmetry of Cu(100)/Nb(100)/α-Al_2O_3 (01$\bar{1}$2). In polycrystalline Nb/Cu multilayers, the hydrogen atoms are localized in the Nb layers, and the concentration decreases with decrease in thickness of the Nb layers below 80 nm. In Nb/Cu multilayer the hydrogen atoms are solved both in Nb and Cu.

Keywords: Nb/Cu multilayer; Hydrogen

1. Introduction

It has been recognized that thin films show different behaviors from bulk systems. Particularly important differences occur with hydrogen incorporation because hydrogen influences the electronic structure and/or relaxes the interfacial strains. A superlattice structure prepared by controlled stacking of thin layers with different substances can introduce a chemical modulation. If we make a choice of similar elements as stacking substances, a smooth modulation of hydrogen can be achieved in a sinusoidal form as shown by Nb/Ta superlattices [1,2]. A sharp modulation can be obtained by stacking thin layers having different solubilities for hydrogen. In this context, hydrogen-induced lattice expansion have been studied recently in Mo/V superlattices and their decrease has been attributed to the biaxial clamping [3]. Another aspect of the modulation is associated with the electron transfer at the interface. The control of magnetic coupling has been studied in the Nb/Fe system [4]. Most of the studies relating to hydrogen modulation have been made in bcc/bcc superlattices probably because of the easiness of first growth, but an extension to bcc/fcc multilayer structures is desirable.

In the present paper, two kinds of studies are described based on the results of ion beam analysis. It will be shown that the hydrogen concentration decreases with decreasing layer thickness below 80 nm in the polycrystalline Nb/Cu system. This result is consistent with ion beam studies [5,6] but not with a diffraction study [7]. The textured Nb/Cu multilayers induce a hydrogen incorporation also in Cu layers, in contrast to the situation in the polycrystalline system.

2. Experimental

Nb/Cu multilayered samples were prepared on α-Al_2O_3 (sapphire) substrates using electron beam evaporation technique under UHV condition. All sapphire substrates were annealed at 1500°C for 24 h in air to eliminate by strain, induced polishing. Nb and Cu films were deposited at the rate of about 0.2 nm/s onto sapphire substrates at 750°C for Nb and at less than 300°C for Cu. After the evaporation, the samples were removed from the UHV chamber into a hydrogenation vessel where they were heated at 300°C in a vacuum of 5×10^{-7} Torr. Hydrogen entered easily the multilayered sample top-covered with Cu. For the ion beam analysis, the samples were exposed to open air and the resulting copper oxides were capable of fixing.

Nb/Cu multilayered samples were analyzed using 3 MV tandem and single-stage accelerator at the TIARA facility in JAERI/Takasaki. The RBS/channeling analysis was

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carried out using $^4He^+$ ions with the energies of 1.5 to 2.4 MeV. The channeling analysis was performed by comparing the spectra under aligned and non-aligned conditions. The thickness of Nb and Cu layers in multilayer sample was determined by heavy ion Rutherford backscattering spectrometry (HI-RBS) using 16 MeV $^{16}O^{5+}$ ions [8]. The detailed hydrogen profiling in the Nb/Cu multilayer was accomplished by employing ^1H (^{15}N, $\alpha\gamma$)^{12}C reasonant nuclear reactions (^{15}N-NRA) [9]. The beam current was about 20 nA, and the beam diameter was 5 mm in diameter. The yield of the characteristic γ-rays of the resonant nuclear reactions was measured as a function of incident ^{15}N ion energy with a 3″ NaI(Tl) detector. The absolute hydrogen concentration was measured by referring to hydrogenerated amorphous Si (14 at.% H) on a Si crystal.

3. Results and discussion

Fig. 1 shows a typical HI-RBS spectrum from a polycrystalline Nb/Cu multilayered sample. Cu layers are equally spaced by inserted Nb layers having thicknesses of 10, 20 and 40 nm respectively going from the top to the bottom. In the higher energy region one can see three well-separated peaks coming from the Nb layers. The peaks in the lower energy region are attributed to the corresponding four Cu layers having a thickness of 20 nm. The Cu peaks show a complicated structure which is caused by the contributions of the various Cu isotopes. The thicknesses determined by the simulation of RBS spectrum are 11, 22 and 44 nm from the top for the three Nb layers, and 28, 35, 36 and 32 nm from the top for the four Cu layers. Thus the HI-RBS spectra demonstrates good mass separation and a reasonable depth resolution in comparison with standard RBS using $^4He^+$ ions.

After H-charging into multilayered sample, the hydrogen profile was measured using the ^{15}N-NRA technique. The distribution of hydrogen on the Nb layers can be clearly observed in Fig. 2. In the upper portion of this figure, a simulated curve is drawn by assuming classical Bohr straggle. The values indicated close to the three peaks indicates the layer thicknesses. In this simulation a uniform distribution of hydrogen within the Nb layers was assumed. The depth resolution in ^{15}N-NRA technique is better than 8 nm. The calculated thicknesses for the Nb layers are 14, 23 and 37 nm from the top, respectively. These values coincide with those obtained by HI-RBS within experimental error. Thus, the hydrogen atoms are not incorporated in a diffuse region at the interface. The obtained concentration profile for hydrogen is shown in the bottom part with the converted scale of depth. The concentrations are in the range of the α-phase and become smaller as the thickness decreases. In this figure one can also recognize the linear decrease of the hydrogen concentration with decreasing Nb thickness. This behavior is observed only in Nb layer thinner than about 80 nm. Judging from published results [10], lattice imperfections can trap hydrogen atoms which increases the local concentration of hydrogen. But in the present case the opposite behavior is observed.

In the following two figures, the growth textured of Nb/Cu layer structure on the $(01\bar{1}2)$ sapphire substrate is shown. The orientational relationship was obtained through mapping the planar channeling points in an angular coordinate system. Fig. 3 illustrates the crystallographic relationship between the Nb single-crystalline layer and the

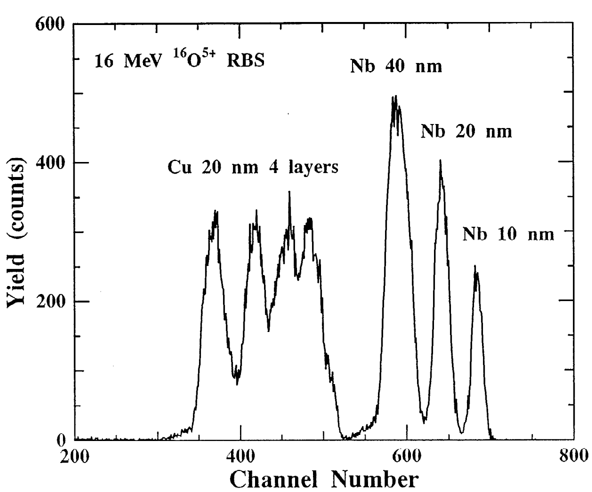

Fig. 1. HI-RBS spectrum of 16 MeV $^{16}O^{5+}$ ions from a polycrystalline Nb/Cu multilayer sample composed of Cu 20 nm/Nb 10 nm/Cu 20 nm/Nb 20 nm/Cu 20 nm/Nb 40 nm/Cu 20 nm on sapphire substrate. The thicknesses here are designed ones.

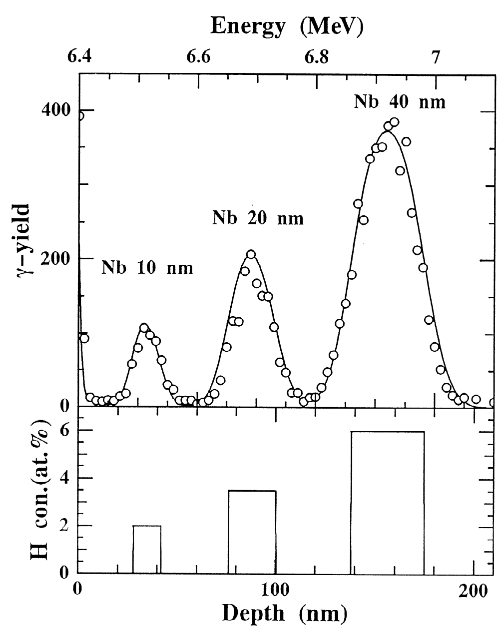

Fig. 2. Hydrogen depth distribution determined by ^{15}N-NRA in a polycrystalline Nb/Cu multilayered sample.

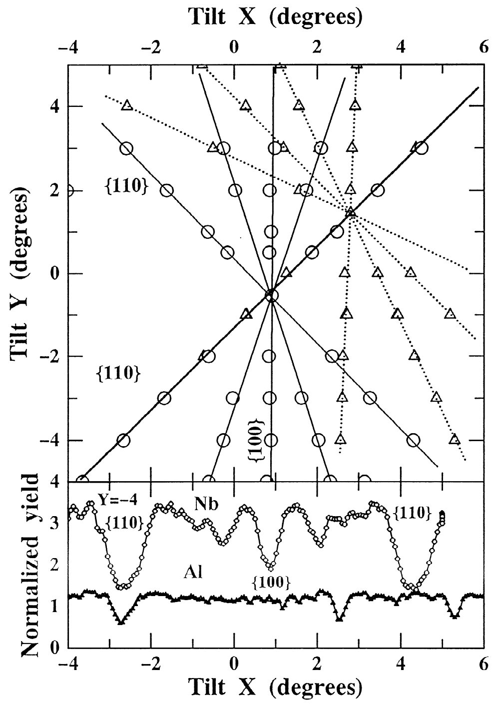

Fig. 3. Mapping of planar channeling points around ⟨100⟩ Nb and ⟨01$\bar{1}$2⟩ sapphire axes in a X–Y angular coordinate system. The lower curves correspond to the linear scanning for Nb and Al of sapphire substrate along X-axis at fixed $Y=-4$. Open circles for Nb and open triangles for Al of sapphire substrate.

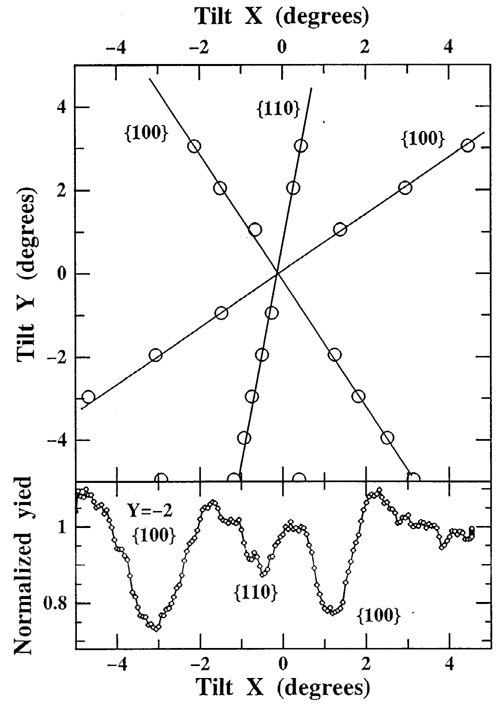

Fig. 4. Mapping of planar channeling points around ⟨100⟩ Cu axis in a X–Y planar coordinate system. The lower corresponds to the linear scanning for Cu along X-axis at $Y=-2$.

(01$\bar{1}$2) sapphire substrate. The dotted lines drawn through planar channeling points denoted by triangles at the upper part correspond to the crystallographic planes about the ⟨01$\bar{1}$2⟩ zone axis of sapphire. The solid lines show the Nb planes about the ⟨100⟩ zone axis. In the lower part, the typical result of scans about the x-axis at $Y=-4$ are shown for the Nb layers and the Al sublattice of the sapphire substrate. From this figure it is clear that the Nb layers are grown in single-crystalline form and that the grown axis of ⟨100⟩ does not coincide with the ⟨01$\bar{1}$2⟩ zone axis of sapphire. The zone axes of Nb and sapphire are on the {110} planes of the grown Nb layer. This relationship is consistent with the results in Nb single crystal growth on sapphire substrates at different orientations (see, for example [11]).

An additional growth of Cu layer on this (100) Nb layer has been tried by lowering the substrate temperature. Fig. 4 shows the mapping of planar channeling points for Cu layer with 250 nm thickness on Nb, suggesting a ⟨100⟩ single crystal or strongly textured growth of Cu. In this experiment it was impossible to obtain the in-plane orientation relationship between the Cu and Nb layers because of the experimental limitations.

Fig. 5 provides evidence for a textured growth of Cu/Nb on (01$\bar{1}$2) sapphire substrate. The crystal quality of the multilayer was examined by RBS/channeling of 1.5 MeV $^4He^+$ ions in order to obtain the isolated spectra without any influence from Nb layer. The crystallographic stacking sequence is descried as follows: Cu (100)/Nb (100)/sapphire (01$\bar{1}$2). The big difference in backscattered yields of Cu layers between random and aligned spectra shows the good crystal quality of layers grown. But the backscattered spectrum from Nb sublayer under ⟨100⟩ channeling conditions is not the continuation of an aligned component in the Cu layer, which implies a strong distortion of Nb lattice after Cu deposition or a misalignment between the Cu and the Nb layers.

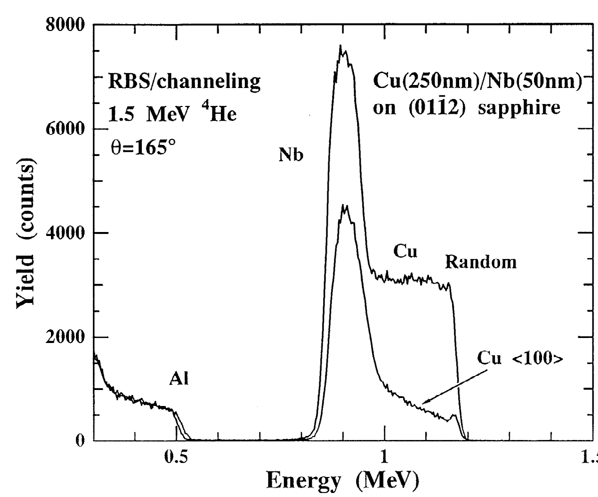

Fig. 5. 1.5 MeV $^4He^+$ RBS/channeling spectra from textured Cu (100)/Nb (100) films on a (01$\bar{1}$2) sapphire substrate. Thicknesses of the Cu and Nb layers are 250 nm and 50 nm, respectively.

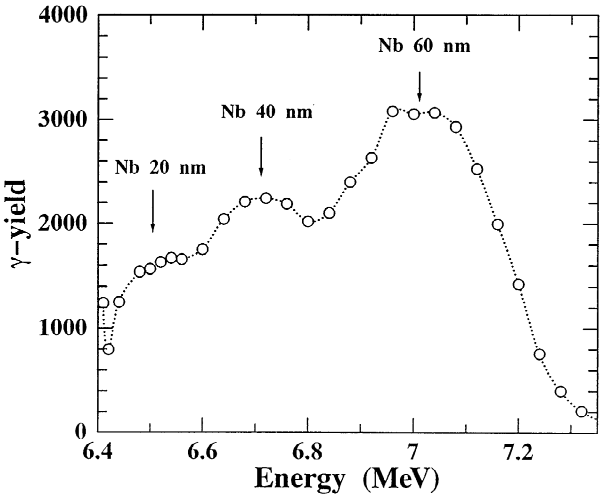

Fig. 6. The result of ^{15}N-NRA analysis of H-charged textured Nb/Cu multilayer composed of Cu 20 nm/Nb 20 nm/Cu 20 nm/Nb 40 nm/Cu 20 nm/Nb 60 nm on (01$\bar{1}$2) sapphire substrate.

Hydrogen was introduced into this sample following the same way as in the polycrystalline sample. Fig. 6 show the hydrogen profile in a multilayer composed of Nb and Cu. The designed thicknesses for the Nb layers are 20, 40 and 60 nm from the top, respectively. The inserted Cu layers have a constant thickness of 20 nm. The estimated hydrogen concentration is within the range of the α-phase. The γ-ray yields obtained from the energy region corresponding to the Cu layers are different from the low concentration results. The present results suggest the incorporation of hydrogen atoms also into the Cu layers, which is surprising from a thermodynamics point of view. Further studies about the crystallographic and electronic structure are needed.

Acknowledgments

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