Compositional Analysis of Hafnium Nitride Thin Films by Backscattering Spectrometry with a Proton Beam

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We measured the energy spectrum of protons backscattered from hafnium nitride thin films by rf magnetron sputtering and evaluated the concentrations of the constituents in the film with an aid of numerical simulation. The spectrum generated by the simulation with such assumption that film consisted only of hafnium and nitrogen did not reproduce the measured spectrum well. It was suggested that the film contains of other light elements such as carbon and oxygen.

1. Introduction

We have been evaluating the quantity of light elements in compound thin films by proton backscattering. One of the difficulties of proton backscattering is that quantitative analysis of the obtained spectrum is not easy, because the scattering cross section varies with the projectile energy. To estimate the quantity of the light elements, we have developed a simulation code that can reproduce the measured spectra [1]. Fairly good agreement was obtained for the evaluation of carbon atoms in amino acid thin film. In this report, we applied the simulation code to characterize the proton backscattering spectrum from hafnium nitride (HfN) thin film to evaluate the composition of HfN thin film.

2. Experimental

HfN thin films were deposited by rf magnetron sputtering. The deposition conditions are as follows: substrate temperature of 500℃, argon (Ar) pressure of 0.6 Pa, RF power of 80 W, deposition time of 20 min, substrate-target distance of 30 mm. A compound target of HfN was used. The substrate was a piece of 525 μm-thick silicon (Si) wafter with a 400 nm-thick silicon dioxide film (SiO_2) on top surface. The spectrum was acquired with the pelletron-type tandem accelerator equipped at Quantum Science and Engineering Center, Kyoto University. The projectile chosen in the present study was a 1.6 MeV proton (H^+). The scattering cross section of 1.6 MeV H^+ to nitrogen (N) is larger than that of Rutherford scattering by a factor of four [2]. Gold (Au) and N signals were used to calibrate the relation between channel number and energy.

3. Results

The obtained spectrum consisted of that of Hf in higher energy part and those of N, oxygen at SiO_2, and Si in lower energy part. Figure 1 shows the experimentally obtained backscattering spectrum in the lower energy part and spectra produced by the simulator. Simulated spectrum did not show good agreement with the experimental spectrum as the dashed line as shown in Fig.1, so far as the film consisted of Hf and N. Discrepancy between the simulated curve and the obtained spectrum from 270 ch to 280 ch would be due to presence of carbon (C) in the HfN film. The dashed curve is slightly below the measured spectrum between 305 and 310 ch would be due to oxygen (O) in the film. The solid curve shown in Fig. 1 was obtained

assuming that HfN thin film consisted of Hf, N, O, and C. Now the simulated curve well reproduced the obtained spectrum. The areal density was 4.5 x 10^{18} cm^{-2} and the compositions of the constituents were 45 at% of Hf, 43 at% of N, 7 at% of O, and 5 at% of C. The analysis revealed that the nitrogen composition of the film was almost unity and that the film contains C and O as impurities. The spectrum around 290 ch corresponds to O in SiO_2. The spectrum of O of SiO_2 did not agree with the simulation; the fitted curve is above the obtained spectrum. The reason for this discrepancy has not yet been clarified.

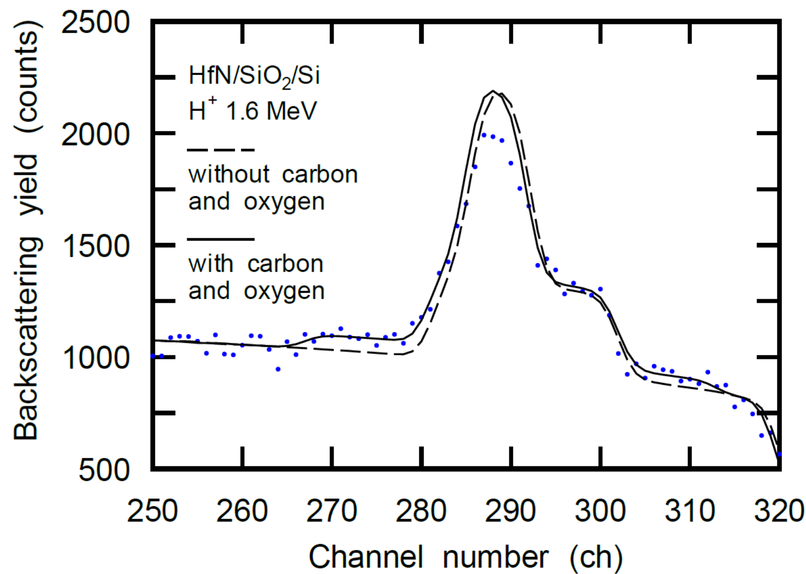

Fig.1 Experimentally obtained backscattering spectrum and fitted curves

4. Discussion

Although discrepancy between the obtained and the simulated spectra was seen for O in the oxidized layer, the simulated spectrum agreed well with the spectrum of the HfN film. In order to check the validity of the present simulation, the spectrum from SiO_2/Si without HfN film was simulated and a good agreement was obtained for this case. The reduction of the dioxide layer was first thought to be a reason for the discrepancy. But the spectra of O with different SiO_2 thicknesses did not show good agreement. Further study is necessary to elucidate the reason for this discrepancy.

5. Summary

We evaluated the composition of HfN thin film by proton backscattering spectrometry. It was proven that the measured HfN thin film consisted of Hf, N, O, and C. The composition of Hf and N of HfN thin film were almost the same. The numerically generated spectrum showed a discrepancy for the oxygen at SiO_2. To confirm the presence of carbon and oxygen, detection of these elements with resonant elastic scattering is necessary.

References

1. Y. Gotoh and M. Nakakami, Quantitative analysis of organic thin films using resonant elastic scattering and numerical analysis, QSEC Annual Report 2019, pp.48-50.

2. Y. Gotoh, W. Ohue and H. Tsuji, Nuclear Instruments and Methods in Physics Research Section B, Beam Interactions with Materials and Atoms. **315** (2013) 68-71.