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Energy dependence of non-Rutherford proton elastic scattering spectrum for hafnium nitride thin film

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ABSTRACT

The energy dependence of the backscattering spectrum of non-Rutherford proton elastic scattering spectrum for a hafnium nitride (HfN) thin film was investigated. The purpose of the study is to demonstrate the feasibility of proton elastic scattering at 1.6 MeV as a tool for compositional analysis of transition metal nitride films on a silicon substrate. A HfN thin film deposited on a silicon substrate was analyzed by a common Rutherford backscattering spectrometry (RBS) with an α beam at the energy of 1.98 MeV, and also by a proton elastic scattering at the energies between 1.53 MeV and 1.61 MeV. The results of two measurements were compared, and a good agreement for nitrogen composition was obtained when the proton energy was higher than 1.59 MeV. It was found that non-Rutherford proton elastic scattering can be used for the compositional analysis of HfN thin films with the thickness up to 230 nm. In analyzing a thicker film, careful observation is necessary.

1. Introduction

Hafnium nitride (HfN) is one of the transition metal nitrides (TMNs), and has excellent properties such as high melting point, high electrical conductivity, strong bonding between the atoms and chemical inertness [1]. We have been investigating several TMN thin films as a material for the cathode of field emitter arrays (FEAs). We found that HfN possesses the lowest work function among the TMNs [2], and the properties of hafnium nitride meet the requirements of the field emission cathode. We have already developed FEAs with the HfN cathode, and excellent properties as an electronic device have been obtained [3]. For further development of such devices, it is necessary to elucidate the material property of the deposited TMN films. One of the major film properties is, of course, nitrogen composition. From the viewpoint of the quantitative analysis of atomic composition, Rutherford backscattering spectrometry (RBS) with a helium (He) ion beam is a powerful tool. The composition can be easily calculated by the ratio of the number of the backscattered ions, taking the difference in the scattering cross sections at the surface into consideration. However, RBS has such a disadvantage that scattering cross sections for light elements are smaller than those for heavy elements. Furthermore, when analyzing a material including a heavy element and a light element, detection of the light element is difficult. It is because the energy loss of the He ions within the material is large, and the spectra of the constituents will be wide. Consequently, the height of each spectrum becomes lower. In many cases, the TMN films are deposited on a silicon (Si) substrate, and the nitrogen (N) signal is superposed on the Si spectrum. Therefore, identification of the N peak becomes more difficult. In order to improve the signal-to-noise ratio, channeling technique is widely used. However, presence of heavy elements in the film does not allow the channeling of the He ion beam, and therefore it is difficult to reduce the signals from the substrate.

In order to improve the sensitivity for the light elements in RBS, use of resonant elastic scattering [4] is one of the good ways. If one uses a proton beam as a projectile, resonant elastic scattering occurs at relatively low energies. Several sharp resonances for N with a proton as a projectile were reported in the literature [5,6]. However, abrupt change of the scattering cross section with the variation of the projectile energy is not suitable for the analysis of the average composition of relatively thick films, except when depth profiling is conducted. To obtain the average film composition, it would be better to choose the condition where the scattering cross section changes gradually with an increase in the projectile energy.

Yang et al. suggested use of a 3.0 MeV proton beam for the detection of light elements, because the scattering cross sections have little energy dependence for light elements at this energy [7]. However, use of the high energy beam may cause radioactivation or neutron production. Surveying the nuclear reaction data, we have selected a proton beam with the energy of 1.6 MeV as a projectile for the non-Rutherford elastic scattering experiments [6]. As compared to the Rutherford scattering, the scattering cross section for N is approximately four times larger, and that for Si is less than half [5,6]. Use of a proton beam is advantageous, because high and narrow backscattering spectrum can be expected owing

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to the lower energy loss. The non-Rutherford proton elastic scattering is thus, an attractive method to derive the composition of the light elements in the film.

However, we have some problems with this method. One of the problems would be relatively large change of the scattering cross section for N, especially between 1.54 MeV and 1.57 MeV. If the film is relatively thick, the change in the cross section leads wrong estimate of the N composition. The reason why we can estimate the film composition by simply comparing the ratio of the total counts of two RBS spectra is that the energy dependences of the scattering cross sections are identical for all elements: inversely proportional to the second power of the projectile energy. Non-Rutherford proton elastic scattering does not always have the same energy dependence with the Rutherford scattering. Therefore, the energy dependence of the N spectrum should be examined in detail. The purpose of the present study is to confirm the feasibility of the non-Rutherford elastic scattering with a 1.6 MeV proton beam for the compositional analysis of TMN thin films on a Si substrate.

2. Experimental conditions

A HfN thin film was deposited by rf magnetron sputtering of a HfN target on <100> oriented Si substrate [2]. The deposition was performed with argon (Ar) gas without adding nitrogen gas. The deposition conditions were: Ar pressure of 0.5 Pa, rf power of 30 W, and the substrate temperature of 400 °C. The deposition time was 10 min.

Backscattering experiments were performed with the tandem-type accelerator "Experimental system for ion beam analysis" which is equipped at Quantum Science and Engineering Center, Kyoto University. The system employs a Cockcroft-Walton type high voltage generator. Proton beams with the energies between 1.52 MeV and 1.61 MeV were used. The scattering angle was 170° in laboratory system and the solid angle subtended by the detector was about 2 msr. The ion fluence for the non-Rutherford proton elastic scattering analysis was 10 μC. In order to check the results of the non-Rutherford proton elastic scattering analysis, Rutherford backscattering spectrometry with an α beam at the energy of 1.98 MeV was also performed with the ion fluence of 40 μC. Use of the higher ion fluence for RBS is to make the N spectrum on Si spectrum clearer. Calibration of the beam energy was not directly conducted, but we estimated the proton beam energy by checking the terminal voltage of the accelerator. The terminal voltage of the accelerator was checked by using $^{16}O(\alpha, \alpha)^{16}O$ resonant elastic scattering near 3.04 MeV [8,9], assuming the resonance at 3.037 MeV, which was obtained by the calculation with SigmaCalc software [10]. The terminal voltage that exhibited the resonant elastic scattering was 7 kV higher than that expected from the resonance energy of 3.037 MeV. Although this is not sufficient for calibration of beam energy, the beam energies are estimated by the terminal voltage, simply subtracting 7 kV from the displayed terminal voltage. The voltage difference of 7 kV may contain ±3 kV error, when we defined the terminal voltage. There would be other factors that add uncertainty of the beam energy, but in this paper, the beam energy will be expressed with the upper three digits of the value estimated in the above procedure.

The counts of the C and N spectra were obtained by subtracting the counts of the background Si spectrum, which was relatively large. Errors in counting the backscattering yields especially for the N spectra were evaluated by standard deviations, which is given by the following equation [11]:

$$\sigma_N = \left(\sigma_G^2 + \sigma_B^2\right)^{1/2} = (N_G + N_B)^{1/2}$$

where σ_N is the estimated standard deviation of the net signal from N, σ_G is that of the gross signal including background, σ_B is that of the signal of the background. The latter two values can be estimated by the gross counts N_G and the background counts N_B, as shown in the above equation. The reason why we adopted this equation is because the background is the Si spectrum, and we could define the background from the entire Fig. of the Si spectrum. We estimated the standard deviation also by Covell method [11,12], where the background is defined by the counts of the several neighboring channels. In the present case, however, the N peak had a neighboring C peak or week O peak, and therefore, determining the background from the neighboring several channels did not work well.

3. Experimental results

3.1. Rutherford backscattering spectrometry with α beam

Fig. 1 shows the RBS spectrum obtained with a 1.98 MeV α beam. The Hf spectrum was isolated from the other spectra and had sufficiently large counts as compared with the background signals. On the other hand, the N spectrum was superposed on the Si spectrum. The net count for the Hf spectrum was 1.02×10^6 and the estimated standard deviation was 1020. The statistical error of the backscattering yield of Hf was 0.1% and negligible. Net count of the N spectrum was 6.02×10^3 with the estimated standard deviation of 479. The statistical error was about 8%. The ratio of the number of the N atoms to that of Hf atoms was calculated to be 0.745 ± 0.059. With the Covell method, lower counts for N spectrum and the estimated standard deviation more than 700 were obtained.

3.2. Non-Rutherford proton elastic scattering measurements

Fig. 2 shows the non-Rutherford backscattering spectra with the 1.61 MeV proton beam. The dashed lines show the energies of the backscattered ions from the C, N, O, and Hf atoms at the sample surface. The signal seen at about 1.15 MeV is from C, and that seen at 1.21 MeV is from N. The counts of these spectra were evaluated to be 3.02×10^3 and 5.33×10^3. The estimated standard deviations for the C and N spectra were 358 and 351, respectively. The statistical errors for C and N were 12% and 7%, and therefore the signals of C and N were intense enough. Incorporation of C from the ambient during deposition often occurs in thin film formation, especially for the deposition system pumped with oil diffusion pump. Also small signal from O can be seen at 1.25 MeV. Although signals from O were detected, the backscattering yield was too low to be estimated. In the following, we will focus on the backscattering yields of N, C and Hf.

Fig. 3 shows some of the magnified N and C spectra obtained at the different proton energies. Blue lines show the C spectra and red lines show the N spectra. Background that was subtracted in the

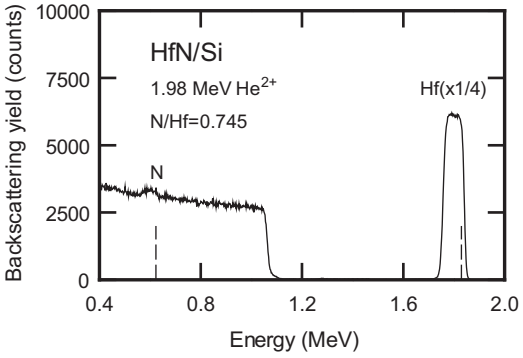

Fig. 1. Rutherford backscattering spectrum taken with a 1.98 MeV α beam.