Transactions of the Materials Research Society of Japan 34[4] 613-615 (2009)

Study of thin-film thickness and density by high-resolution Rutherford backscattering spectrometry and X-ray reflectivity

Amane Kitahara, Satoshi Yasuno and Kazuhisa Fujikawa
Electronics Technology Department, KOBELCO RESEARCH INSTITUTE, INC.,
1-5-5 Takatsukadai, Nishiku, Kobe, 651-2271, Japan
Fax: 81-78-992-6143, e-mail: kitahara.amane@kki.kobelco.com

High-resolution Rutherford backscattering spectrometry (HR-RBS) and X-ray reflectivity (XRR) are both powerful tools that can be used to investigate thin film structures with the same depth resolution. HR-RBS can be used to analyze low-density contrast films since it reveals the chemical composition in films. The elemental information aids the XRR analysis of films containing localized hydrogen atoms and low-electron-density contrast layers.
Key words: high-resolution RBS, X-ray reflectivity, high-*k*, diamond-like carbon

1. INTRODUCTION

X-ray reflectivity (XRR) and Rutherford backscattering spectrometry (RBS) have already been used successfully to study thin film structures and characterize their film thickness, composition, roughness and density. XRR can be used to quantify electron density distribution and film thickness, but not the elemental compositions. On the other hand, RBS can be used to quantify chemical composition and areal density (atoms/cm^2), but not the absolute thickness without a known volume density (g/cm^3) [1]. The two methods thus provide complementary information that can be used for thin film analysis. We present XRR and high-resolution RBS (HR-RBS) analyses of two systems: (1) HfO_2 (0.5-6nm thick) on SiO_2/Si and (2) diamond-like carbon (DLC) film on a bare Si wafer. We then discuss the advantages of each method.

2. EXPERIMENTAL

XRR measurements were performed using a Rigaku SmartLab system with Cu-*K*α radiation. HR-RBS measurements were carried out with 450keV He^+ ions using a Kobe Steel HRBS500 system equipped with a high-stability Cockcroft-Walton-type high-voltage generator and a high-resolution energy analyzer (~0.15%) [2-4].

We prepared two types of thin films. For the first type, HfO_2 and SiO_2 were deposited on Si(001) substrates by atomic layer deposition. Nominal thicknesses of 0.5, 1, 2, 4 and 6 nm were deposited for the HfO_2 on a 1-nm-thick SiO_2 layer on the Si substrate. These are labeled HfO_2~0.5 nm, ~1 nm, ~2 nm, ~4 nm, and ~6 nm, respectively. For the second type, a DLC film was deposited on a bare Si wafer by electron cyclotron resonance CVD.

3. RESULTS AND DISCUSSION

3.1 $HfO_2/SiO_2/Si$

Figure 1 shows the HR-RBS spectra of the $HfO_2/SiO_2/Si$ series. The peaks of three elements (Hf, Si, and O) were observed individually in the spectra. The width of the peaks indicated the relative thickness. We obtained the thickness of each HfO_2 and SiO_2 layer

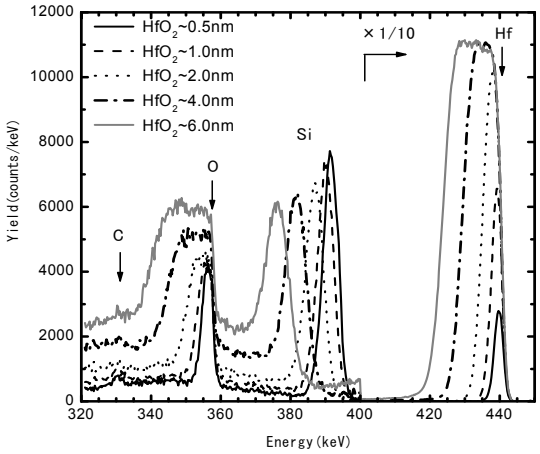

Fig. 1. HR-RBS results of $HfO_2/SiO_2/Si$ systems. Widths of Hf and O peaks correspond to their thickness under the surface.

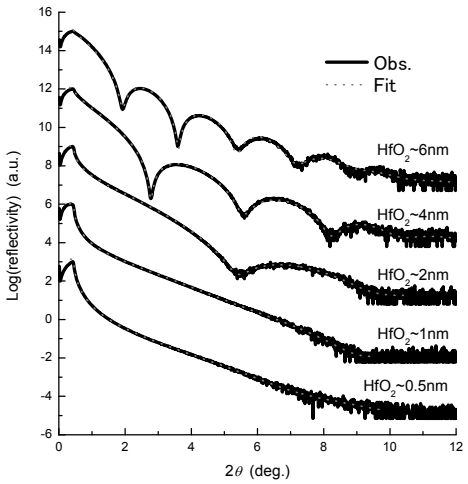

Fig. 2. Measured and fitted XRR of $HfO_2/SiO_2/Si$ systems.

Table I
Obtained thicknesses of HfO_2 layer and SiO_2 layer on a Si substrate by HR-RBS and XRR methods.

Sample: HfO_2~	HR-RBS		XRR	
	HfO_2 thickness (nm)	SiO_2 thickness (nm)	HfO_2 thickness (nm)	SiO_2 thickness (nm)
~0.5 nm	0.21	1.39	1.20	1.16
~1.0 nm	0.60	1.47	0.78	1.08
~2.0 nm	1.53	1.33	1.72	1.00
~4.0 nm	3.16	1.42	3.27	0.96
~6.0 nm	4.77	1.19	4.92	2.00

from curve fitting procedure and replacing the estimated areal densities (atoms/cm^2) with the bulk volume densities (9.68 g/cm^3 and 2.20 g/cm^3, respectively). Width of the Hf peaks indicated the HfO_2 thicknesses. The O peak in SiO_2 was determined by subtracting the O peak in HfO_2 from the total O peak, since the O peak was composed of the two oxide layers. Then, the SiO_2 thickness was calculated.

Figure 2 shows XRR data corresponding to the HR-RBS spectra given in Fig. 1. The density contrast between HfO_2 and Si affected the visible XRR oscillations, whereas SiO_2 layer did not feature remarkable oscillations because of the low-density contrast and very thin film. However, the oscillation periodicity changes did not indicate only HfO_2 film thickness changes, but also the SiO_2 film thickness. We calculated thicknesses of the top of the HfO_2 film and the interfacial SiO_2 film using XRR simulations. Then, we imposed the existence of the HfO_2 and the SiO_2 layers on the simulation models. The thicknesses calculated by HR-RBS and XRR are shown in Table I.

XRR can be used to evaluate the HfO_2 thicknesses with high accuracy due to high-density contrast. The thicknesses of HfO_2 layer obtained by HR-RBS were almost equal to the thicknesses obtained by XRR, except for HfO_2~ 0.5nm. However, it is not as sensitive when measuring the thin and low-density contrast between the SiO_2 layer and the Si substrate with laboratory X-ray equipment. The SiO_2 thicknesses obtained by XRR did not converge on a stable value when least-squares fitting procedure was carried out. On the other hand, HR-RBS could detect a very thin film such as a low-density contrast. Hence, we could confirm the thicknesses of SiO_2 on the XRR simulations.

3.2. Diamond-like carbon film on Si

Figure3 shows the elemental depth profile of a DLC film on a Si wafer obtained from HR-RBS analysis and elastic recoil detection analysis (HR-ERDA) for hydrogen atoms. There existed localized Fe and Ar atoms at the interface between carbon and Si. The Fe atoms remained as contaminants in the chamber since DLC films were usually prepared by deposition on a steel plate as a hard coating. XRR also detected a high-density layer at the interface of the sample, as shown in Fig. 4. The depth (nm) - density (g/cm^3) profile of the DLC film was obtained by fitting the measured XRR using a multiple carbon layer model. However, we could not determine the existence of Fe and Ar at the interface using only the XRR method. In Fig. 4, we recalculated the depth-density profile replacing the chemical

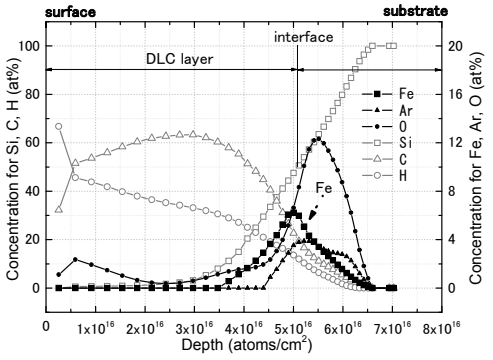

Fig. 3 Elemental depth profiles of H, C, O, Si, Ar, and Fe near DLC surface and interface estimated by HR-RBS.

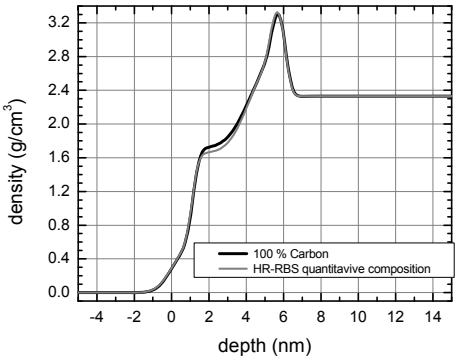

Fig. 4 Depth vs. density profile of DLC film on Si determined by XRR.

composition estimated by HR-RBS and HR-ERDA with carbon. The recalculated profile had a low density near the surface due to concentration of hydrogen.

The electron density obtained by XRR can be converted to the volume density using chemical components in the DLC films obtained by HR-RBS. Furthermore, the converted volume density converts the thickness of layers described in units of 'atoms/cm^2' into units of 'nm' for the HR-RBS results. Then, we can verify the film thickness using both methods.

4. SUMMARY

We demonstrated two examples of thin film analyses through XRR and HR-RBS measurements. The two methods can be used to non-destructively measure film thicknesses on a substrate with sub-nanometer resolution. When conducting XRR using laboratory equipment, it is advantageous to independently quantify the film thickness and electron density, except for systems with low-density contrast of less than ca. 5 %. HR-RBS analyzes the localization and interdiffusion of elements in thin film layers even if the system consists of low-density contrast and includes hydrogen.

REFERENCES
[1] W. K. Chu, J. W. Mayer, M.-A. Nicolet, "Backscattering Spectrometry," Academic Press, New York (1978).
[2] K. Kimura, M.Kimura, Y. Mori, M. Maehara, H. Fukuyama, AIP Conf. Proc., **475**, 500-503 (1999).
[3] C. Ichihara, N. Kawakami, S. Yasuno, A. Hino, K. Fujikawa, A. Kobayashi, M. Ochi, H. Gotoh, T. Kugimiya, Micron., **40**, 66-69 (2009).
[4]http://www.kobelco.co.jp/technobook/p238_e.htm.

(Received July 14, 2009;Accepted Septmeber 24, 2009)