X-RAY REFLECTIVITY MEASUEMENTS FOR DEPTH DENSITY DISTRIBUTION IN THERMAL OXIDE THIN FILM ON SILICON (100)

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Abstract:
X-ray reflectometry (XRR) is a powerful tool for the structural characterization of thin films. However the standardized protocols of the measurements and their analyses need to be established for the reliable and reproducible characterization. The collaborative work between National Institute of Standards and Technology (NIST, USA) and National Metrology Institute of Japan (NMIJ, Japan) for thickness evaluation by XRR has been carried out in order to support the activities for the standardization of the thickness evaluation. In order to evaluate the accurate thickness of thin film structures by XRR experiments, the appropriate model construction of the structures should be required for the XRR data analysis. However there have been numerous discussions about the structures especially around the film/substrate interface. We tried to clarify a depth density distribution of a thermal oxide thin film on a Si substrate by comparing the XRR results obtained from several films which were oxidized by different processes.

Keywords: X-ray Reflectivity, XRR, Thickness, Density, SiO_2 film

1. INTRODUCTION

A continual progress of characterization methods for materials based on nanotechnologies has been required in production and R&D fields [1]. One of the most fundamental structures of the nano-materials is thin and multilayer films and then their thicknesses are one of the key parameters for their properties as well as their composition, density and surfaces/interfaces roughness of each layer. The standardization is a means of the global prevalence of the thickness measurement techniques with accuracy, precision and stability in order to support the progress of the nanotechnologies. In order to establish the standardization of thickness measurements of thin and multilayer structures with nanometer order accuracy, it is important to share the procedure of the measurements, of the analysis of obtained data, and of the calibration of their apparatus for the quality control. However, in general, the practical know-how in the measurements and the analysis is accumulated by only individuals or limited communities. In addition, there are few standards for these procedures and the increase in the number of standard materials for thickness measurements is small.

We have been studied in order to improve the thickness measurement techniques with high accuracy and precision and then to develop the standard materials for the thickness measurements employed by X-ray reflectometry (XRR) because of its possibilities of nondestructive and precision measurement with high sensitivity. In addition, the traceability source of the evaluated thickness is a clear. We have succeeded in development of XRR system and in supply the thickness standard materials (NMIJ Certified Reference Materials (CRM) [2]) consisted of thin and multilayer film structures. The main sources of the uncertainty of thickness evaluation by high performance XRR system are not originated from the mechanical accuracy, precision and stability of the apparatus but from the imperfection of samples. A model structure for the calculation in order to evaluate the thickness from XRR profiles in the analysis process is required. The accurate thickness evaluation can not be performed without the fine information of the structures for the film structures. However there have been numerous discussions about the structures especially around the film/substrate interface. In this work, we tried to clarify a depth density distribution of a thermal oxide thin film on a Si substrate by comparing the XRR results obtained from several films which were oxidized by different processes.

2. EXPERIMENTS

The XRR system is installed a powerful X-ray generator (18 kW) equipped with Cu rotating anode. The beam is collected to form a parallel beam by a parabolic multilayer mirror and then is compressed and monochromated by a crystal mirror for X-ray. Three types of crystal mirror are installed in this system. They can be selected in Ge(111) and Si(111) channel-cut crystal monochromator and Ge(220) 4-bounce monochromator combined with incident slits. The X-ray intensity is collected by a Si avalanche photodiode detector (APD) with reception slits or an analyzer crystal (Ge(111) channel-cut crystal) which can be selected as appropriate resolution. The wide range measurement more than 10^8 dynamic range can be realized by the employing the X-ray generator and the APD. In this work, all XRR profiles were obtained with Ge(111) monochromator and the reception slit collimation mode.

The most important parameters for a thickness measurement by XRR are X-ray wavelength and angle scan control for axis around sample (ω) and detector (θ). The quality of X-ray is able to be confirmed by X-ray diffraction peak from crystalline structure materials with high completeness, namely, Si crystal. On the other hand, the developed XRR system is realized the angular scan control with 0.00002° precision by adopting both high-resolution

encoders and closed-loop feedback control systems for ω and θ axis. However the accuracy of the angular scan is affected by not only the precision of the encoders and the control systems but also the eccentricity originated from the declination between rotational center and the gravity center at the mounting position after the assembling. Therefore the system has a function for calibration of the angular scan after the assembling the encoders. In order to make clear the uncertainty of the angle control, the system is employed similar calibration method to the Japanese national angle standard by simplifying [3]. The max value of the correction at the each point is 5 sec with the uncertainty of ±1 sec. The precision of the system is as noted below. The divergence of X-ray (Cu Kα1) through the Ge(111) channel-cut crystal optics system is $\Delta\lambda/\lambda = 10^{-4}$. The evaluated thickness is affected by the divergence and the estimated value is 0.02% of the thickness of the films. The value for the 10 nm-thick samples is 2×10^{-3} nm. The angle scales of encoder which controls the angle scan of ω and θ axis. The max value of the calibration is 5 sec for the instrument reading with the uncertainty of ±1 sec. The estimated uncertainty affected by the angular scan is 2×10^{-3} nm on the assumption that the difference of the thickness evaluated by before and after the angle calibration is uncertainty for the scan. The Si APD type detector has an enough wide measurement scale and dynamic range for the collimated X-ray beam. The linearity of the detector has little effect on the thickness evaluation. The repeat accuracy of the thickness evaluation by XRR depends on the stability of samples. In case of a GaAs/AlAs superlattice sample (3 pairs, 9.5 nm each layer thickness), the reproducibility estimated by a duplicated measurement is 10^{-3} nm for the most inside AlAs layer on the GaAs substrate. From the above reason, the precision of the XRR system is extremely high and the uncertainty of thickness evaluation induced by the measurements for the thin films structure with sub-nm layers reaches 10^{-3} nm range.

The alignment between the incidence X-ray beam and the sample position is extreme important for the precision measurement. The alignment is performed precisely by the method using analyzer collimation mode [4].

In this work, two types thermally oxidized thin films (SiO_2) on Si(100) substrates were used for the samples. One was grown at 1000 °C with slow ramping (SR) process by using an electric resistance heater. Other sample was grown at 850 °C with rapid anneal (RA) process by using an infrared lamp. The rising rates of SR and RA process were 30 °C/min and 100 °C/sec, respectively. In both process, the thermal-oxidation was performed in a quarts-tube furnace in a dry O_2 flow at atmospheric pressure. The RA process system was developed newly in order to investigate the affection for growth of SiO_2 films by both the growth temperature and the rising rate.

2. RESULTS

In our previous work [5], XRR experimental results indicated the followings. (i) SiO_2 thin films oxidized by SR and RA process were consisted of a two-layer structure, namely, a dense transition layer around 1 nm thick near the SiO_2/Si interface and an overlayer on the transition layer. (ii) In the SR process, the values of density of overlayer and transition layer, which formed lower temperature, were higher than those which formed higher temperature. (iii) The RA samples grown at 1000 and 1100 °C had a lower density layers compared with the SR samples grown at 750 and 1000 °C. The density of the transition layer of the SR 1000 °C sample was almost 3% denser than that of the RA 1000 °C.

From these results, we assumed that the difference of density for the SR and the RA samples was affected by the starting temperature of the oxidation. In case of the SR process, SiO_2 films growth was started less than 750 °C because of its slow-rising rate of temperature. On the other hand, the low-temperature oxidation was difficult to occur by the RA process and then SiO_2 film was grown at around the growth temperature. It means that the rising rate is an important parameter for the density control of SiO_2 films.

Here we just show a comparing result for SR 1000 °C sample and RA 850 °C sample in order to demonstrate that the above assumption. Figure 1(a) shows XRR profiles for

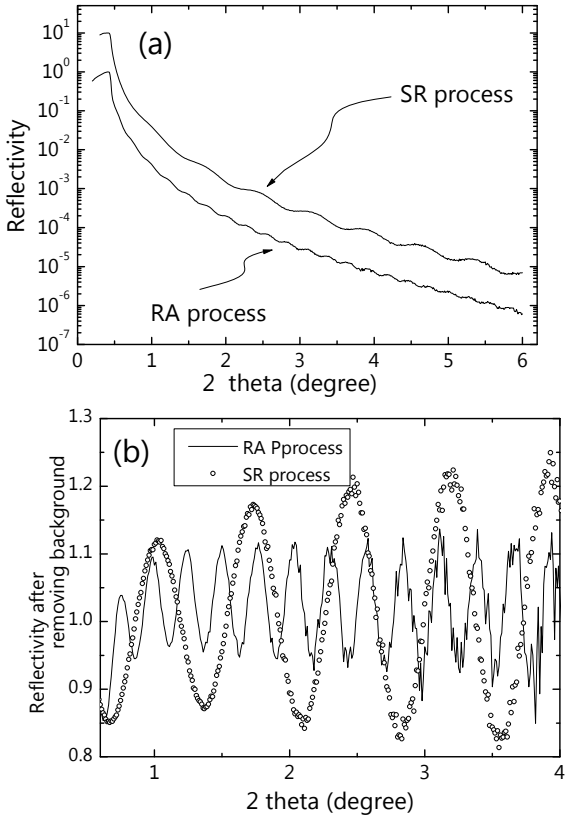

Fig. 1: (a) Comparison between X-ray reflectivity profiles obtained from the samples oxidized by slow ramping (SR) process at 1000 °C and rapid anneal (RA) process at 850 °C. (b) the profiles after removing the background.

the SiO_2 films, which oxidized by SR process at 1000 °C and RA process at 850 °C. From this figure, it is clear that the periodicity of the profiles is different remarkably. This phenomenon in XRR profiles indicates the thickness difference of them. In order to emphasize the difference of these, each profile is plotted after removing the background in Fig. 1(b). In this figure, it is shown that the profile of the

SR process sample has higher amplitude in the oscillation than one of the RA process sample. The oscillation amplitude corresponds to relative density contrast among layers in film structures. There exists has a higher density contrast among layers including the substrate in the SR process sample than the RA process one.

Table 1: Analysis results of the XRR profiles obtained from the samples oxidized by rapid anneal (RA) process at 850 °C and slow ramping (SR) process at 1000 °C and

Temperature rise process	Growth Temp. (°C)	Thickness (nm)	Density (g cm^{-3})	
			Overlayer	Transition layer
RA	850	12.3	2.28	2.39
SR	1000	32.6	2.30	2.46

Table 1 is summarized the analysis results of the XRR profiles obtained from the samples oxidized by slow RA process at 850 °C and SR process at 1000 °C, as shown in Fig.1. This result shows that the SR sample has denser transition layer. The density value is 2.46 g·cm^{-3}. The density of the transition layer of the SR sample is almost 3% denser than that of the RA. These values show good agreements with our previous result [5]. On the other hand, the density values of the overlayer and the transition layer of RA samples values are 2.28 and 2.39 g·cm^{-3}, respectively. These values obtained from RA 850 °C sample are reasonable compared with those of RA 1000 °C sample and RA 1100 °C sample [5]. This fact indicates that the rising rate is an important parameter for the density control of SiO_2 films. It is confirmed that even if the oxidation is carried out at low-temperature (850 °C), the denser transition layer dose not grow by RA process (100 °C/sec).

3. CONCLUSION

We have investigated depth density distribution of a SiO_2 thin film on a Si substrate by comparing the XRR analysis results obtained from several films which were oxidized by different processes. In this work, we demonstrated that the rising rate is an important parameter for the density control of SiO_2 transition layer by comparing the results for the samples oxidized by slow ramping (SR) process at 1000 °C and rapid anneal (RA) process at 850 °C. By avoiding the low-temperature oxidation at less than 750 °C by RA process, the growth of the denser transition layer is suppressed.

ACKNOWLEDGEMENTS

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REFERENCES

[1] The International Technology Roadmap for semiconductors, 2013 edition, Metrology, http://www.itrs.net

[2] NMIJ CRM5202-a SiO_2/Si multilayer film and 5204-a GaAs/AlAs superlattice, http://www.nmij.jp/english/service/C/

[3] T. Watanabe, H. Fujimoto, and T. Masuda, “Self-Calibratable Rotary Encoder”, *J.Phys.cof.Ser*., vol.13, pp. 240-245, 2005.

[4] K. Omote and Y. Ito, “Thermal Expansion Low Dielectric Constant Thin Films by High-Resolution X-Ray Reflectivity”, *Mater.Res.Soc.Symp.Rroc*, vol.875, pp. 223-228, 2005.

[5] K. Odaka, A. Kurokawa, Y. Azuma, Lulu Zhang, and T. Fujimoto, “Density Profile of Thermal Oxide Thin Films on Si(100)”, *Jpn.J.Appl.Phys*., vol.51, 091301, 2012.