Preparation of SiO_2/Si Multilayer Thin Film and its Usage as a Standard Reference Material for Depth Profiling

I. Kojima*, N. Fukumoto, T. Fujimoto, B. Q. Li and H. Takaya

National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan

(Received October 7 1998; accepted January 13 1999)

A multilayer thin film with a SiO_2(20.4 nm)/Si(20.8 nm)/SiO_2(21.0 nm)/Si(20.9 nm)/SiO_2(21.3nm)/Si(001) structure was prepared by the rf-magnetron sputtering method in an ultrahigh vacuum system. The X-ray reflectivity measurements have been carried out to determine the structural properties such as layer thicknesses, densities, and surface and interface roughnesses. The Auger depth profiling of the multilayer film and the commercially available thermal oxide film, SiO_2 (101.6 nm) /Si were compared by using 1keV Ar ions. The depth resolutions obtained at the 5 interfaces of the multilayer film were in the small range of between 1.9 and 2.4 nm. The change of the depth resolution with an increase of sputtered-depth was very small. In addition, the 5th interface depth resolution of the multilayer film, 2.4 nm was almost consistent with that of the thermally oxidized film, 2.3nm. The high resolution in depth profile of the multilayer films, which is close to that of electron escape depth, is discussed with regards to conformal film growth. The multilayer film reported here is shown to be useful for the optimization of depth profiling as a reference materal.

1. INTRODUCTION

The development of advanced ULSI processing techniques requires a high resolution surface chemical analysis to ensure the process' capability. An excellent depth resolution on the nm level should be achieved for the usual composition depth profiling, because the thickness of ultrathin gate oxides for high-performance semiconductor devices will be scaled down to the order of nm [1].

In order to calibrate the thickness in depth profiling for surface chemical analysis, the reference materials such as single layer and multilayer thin films are employed. So far, single layer Ta_2O_5/Ta [2] and SiO_2/Si [3] films and a multilayer Cr/Ni film [4] have been supplied from governmental institutes as national standards. Recently, the ISO/TC201 Subcommittee on Depth Profiling has discussed the usage of superlattices like GaAs/AlAs and multilayered thin films for the optimization of sputter depth profiling by surface chemical analysis [5].

Since the sputtering rate by ions depends strongly on the material, it is desirable that the reference materials possess properties similar to the materials being analyzed. Furthermore, sharp interface and reliable thickness values are the important features for the precise depth profiling.

To cope with these demands, we aim to develop standard reference materials such as the mulitilayered SiO_2/Si films. In the previous paper, we briefly presented a comparison between the depth profiles of a multilayer thin film deposited on a Si(111) wafer and a commercially available thermal oxide film [6]. Here, we present the details of the preparation of the multilayer film, its structural analysis by X-ray reflectivity, and its usage as a reference material for Auger depth profiling

2. EXPERIMENTAL

The SiO_2/Si multilayer thin films were deposited in an ultrahigh vacuum (UHV, base pressure $1x10^{-8}$ Pa) rf magnetron sputtering system, which consists of three rf sputtering guns and one rf radical gun. The sputtering gun is carefully aligned to 35° offset from the substrate normal and 60 mm offset from the substrate center. With this special design an excellent film thickness uniformity, which has less than 1% deviation in thickness over a 3 inch wafer, can be achieved. N-type Si(001) wafers, 3 inch in diameter

and 380 μm in thickness, were first ultrasonically cleaned in acetone for 5 min. The native oxide on the wafer was removed by rinsing in 2.5% HF solution and then in ultrapure water. Under the UHV condition, the wafers were further heated to 430°C for 30 min to further clean it. When the temperature reduced to 310°C, the deposition was started. The SiO_2 and the Si layers were deposited from pure SiO_2 and Si targets, respectively. The sputtering power and the Ar gas flow were 300W and 15 sccm [7] for both SiO_2 and Si depositions. The layer thickness was controlled by selecting a suitable deposition time.

X-ray reflectivity measurements were performed using a high-resolution x-ray diffractometer (Rigaku SLX-2000). A rotating anode Cu Kα source (18kW) was used and the X-ray beam was monochromatized by using a Ge(220) double-crystal monochromator. The incident and reflected beams were collimated with 50 μm slits and the reflection intensity was measured by a scintillation counter. The 2θ angular resolution of the instrument is 0.0002°. The specular reflectivity curve was recorded with a θ-2θ scan.

3. RESULTS AND DISCUSSION

It is well known that the refractive index for X-ray wavelengths is slightly less than unity, i.e. $n = 1 - \delta - i\beta$, and consequently the total external reflection occurs at very low incidence angles (θ) smaller than a critical angle θ_c, which is related to the real part of the refractive index by $\theta_c = (2\delta)^{1/2}$. In the region above the critical angle, the X-ray beam penetrates successively deeper into the films as the angle is increased. If the densities of thin films are different from that of the substrate, interference oscillations (Kiessig fringes) are observed in the reflectivity profile. Theoretically, the amplitude of the oscillations is proportional to the density differences, the periodicity of the oscillations equals 2θ/thickness, and the general decay of intensity is due to the surface and interface roughness. The accuracy of the X-ray reflectivity measurementts was described elsewhere [8-10].

Figure 1 shows the experimental (dotted line) and fitted (full line) reflectivity profiles. The structural parameters of the sample, such as the optical constants, the layer thickness and interfacial RMS roughness were deduced from the data by means of a nonlinear least-squares curve-fitting technique. In the curve-fitting process, suitable initial values (depending on the materials and deposition conditions) were selected for the optical constants, layer thickness and interfacial roughness. As the fitting proceeded through iterations, these quantities were cotinuously adjusted and finally reached their optimum values. It should be mentioned that we set the following conditions: all SiO_2 layers constrained to the same optical value, and as were the Si layers. However, the optical constants for the Si layer are not necessarily same as that for the Si substrate since the Si film may have different density from the Si substrate. To improve the fit of the experimental data and on the base of our previous study [11], we introduced an interface layer between the Si substrate and the 5th SiO_2 layer, whose density is different from that for both SiO_2 and Si. The results obtained are summarized in Table I.

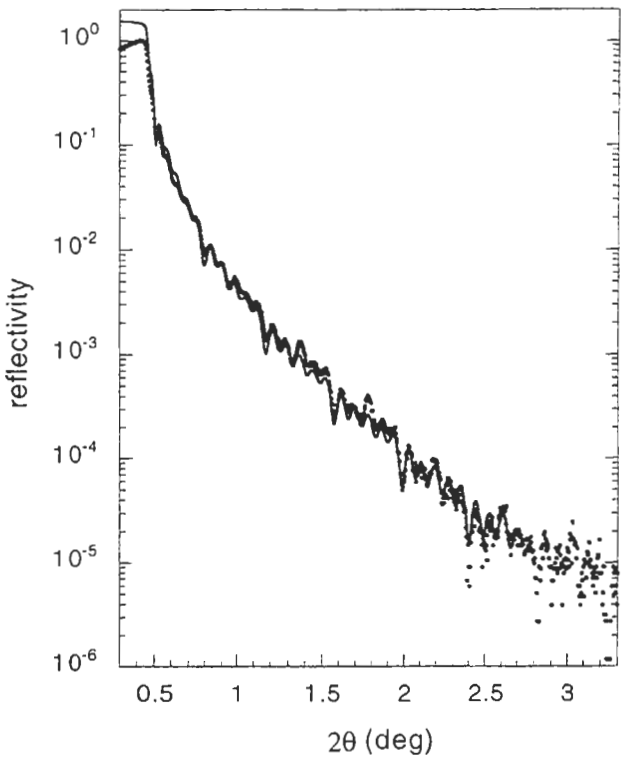

Figure 1 X-ray reflectivity profile of the SiO_2/Si multilayer film. The dotted and solid curves show the experimental and theoretically fitted profiles, respectively.

Figure 2 shows the X-ray reflectivity data of a thermal oxidized SiO_2 thin film (purchased from JEOL Ltd.). The optical constants, the film thickness, and the surface and interface roughness can be readily obtained from fitting the experimental data. The thickness of the thermal oxidized SiO_2 thin film was determined to be 101.6 nm with an accuracy better

Table I. Structural parameters for the SiO_2/Si multilayers ascertained from the XRR .

Layer	Density(g/cm3)	Thickness(nm)	RMS roughness(nm)
SiO_2	2.24	20.4	0.65
Si	2.33	20.8	0.18
SiO_2	2.24	21.0	0.70
Si	2.33	20.9	0.08
SiO_2	2.24	20.3	0.61
interface(SiO_2)	2.43	1.0	0.38
Si (001)	2.34 *	10000*	0.36

* These values are fixed during optimization.

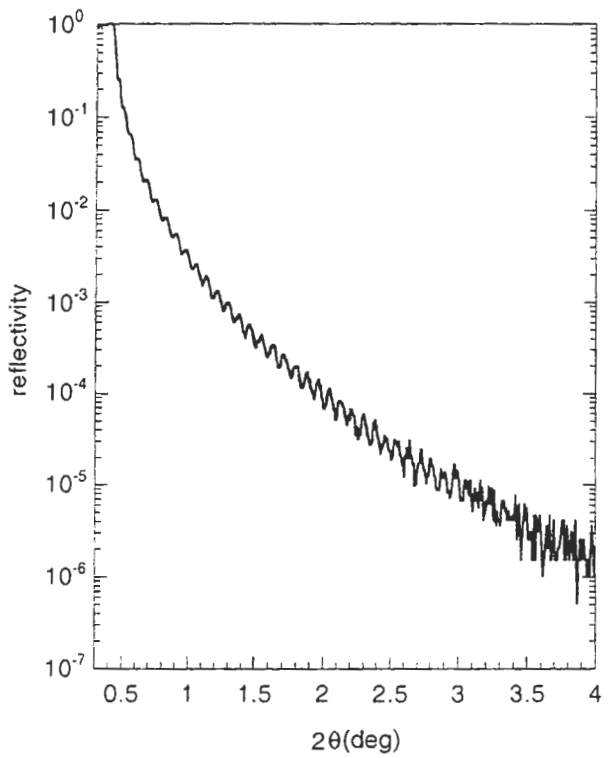

Figure 2 X-ray reflectivity profile of the thermally oxidized SiO_2 film.

than 0.5%.

Figure 3 shows the Auger depth profiles of the multilayer and the single layer films. Measurements were carried out with 1 keV Ar ions and at a glancing incidence angle of 35°. The experimental profiles were recorded by plotting the peak-to-peak intensities of lock-in differential measurements for the Si LVV and O KLL Auger signals. The normalized intensity plots of the two signals are shown in Figure 3. No other contaminant element was detected except for carbon on the top surface. The averaged sputtering rates were almost the same for each sample; 1.50 nm/min for the multilayer and 1.48 nm/min for the single layer films, respectively. This is related to a very small difference in sputering rate between Si and SiO_2. The abscissa of Figure 3 is related to these rates.

Figure 4 shows the change in depth resolution calculated from O KLL plots by using the 84-16% definition with increasing thickness. The depth resolution of the multilayer film changed from 2.2 nm for the first SiO_2/Si interface to 2.4 nm for the bottom (5th) interface. The 5th interface depth resolution of the multilayer film was almost consistent with that of the thermally oxidized film.

It is well known that the depth profile broadening at each interface results from several effects, such as, the sputter-induced roughness, electron escape depth and atomic mixing [11]. For example, the escape depth of an O KLL Auger electron is about 1.5-1.7 nm. It is usually believed that the interfaces of thermally oxidized films are atomically flat [13]. Since the depth resolutions of these two samples almost coincide with each other, the roughness which could exist in the interfaces of the multilayer is rather small and does not affect the broadening of depth profile. This is because the film growth occurs almost conformally, which means that the initial surface roughness of the clean Si surface appears on the top surface even after multilayer deposition. X-ray reflectivity data which shows a small change of the interface roughnesses with increasing number of layers supports this view.

In the previous paper, we reported the observation that the depth resolution of the multilayer film fabricated on the Si(111) wafer increased with an increase of sputtering depth [6]. Since the depth resolution obtained from the thermally oxidized film was almost identical to that obatined from the multilayer at the same thickness, it is suggested that the adjustment of the ion beam focusing was insuficient for the last measurement. This also ensures that the

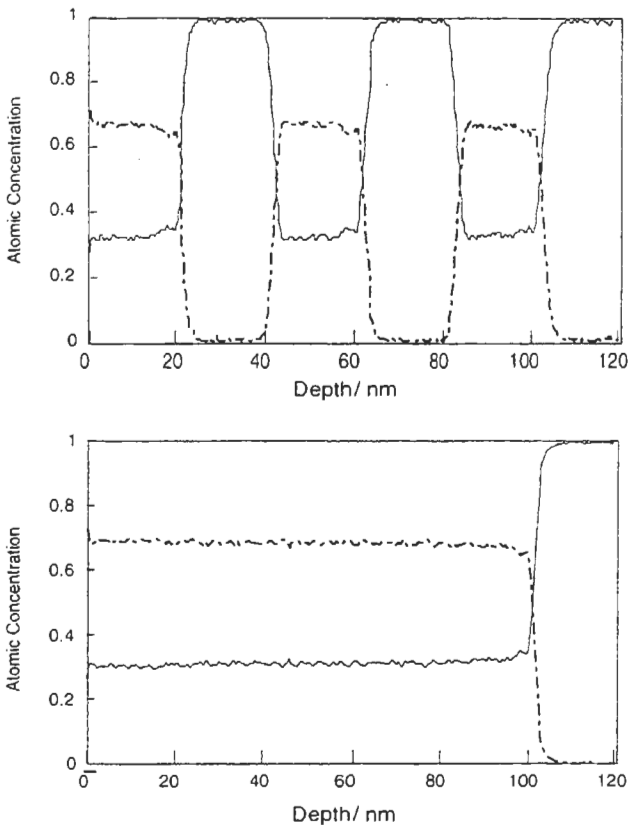

Figure 3 Auger depth profiles of the SiO_2/Si multilayer film and the thermal oxide film. The solid and dot-dashed lines show the Si LVV and O KLL intensities, respectively.

well understood multilayer film is convenient to check the equipment conditions for the depth profiling analysis.

The depth resulutions of both the 2nd and the 4th interface, SiO_2/Si interface, were a little smaller than those of the other 3 interfaces, Si /SiO_2 interface. This is not due to the interface roughness effects considering that the smaller roughnesses are obtained in SiO_2/Si interfaces from the X-ray reflectivity. Further studies are necessary to clarify the effects by the three factors stated above to explain the observations. However, the difference in inelastic electron mean free paths between two materials, about 0.3 nm [14], is likely to account for most of the difference of the depth resolution.

4. CONCLUSION

In conclusion, the SiO_2/Si multilayer film prepared by the rf-magnetron sputtering method yielded a high depth resolution for Auger depth profiling The depth resolution was about 1.9-2.4 nm which is comparable

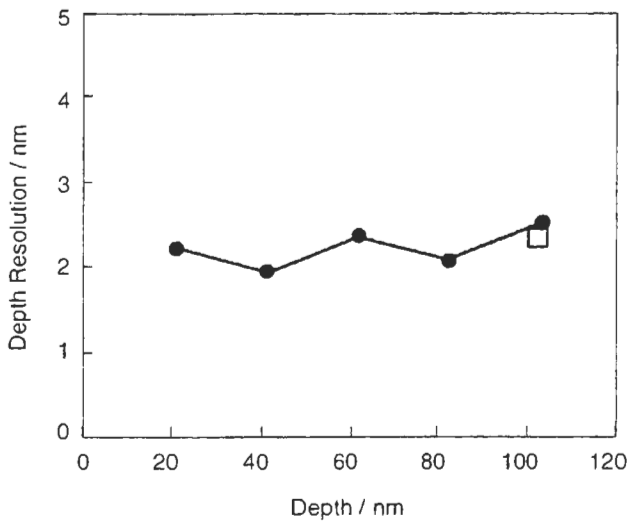

Figure 4 The change in depth resolution with increasing depth. The solid circles show the data obtained from the multilayer interfaces, and the rectangle shows the data of the thermal oxide film.

to the electron escape depth, and almost constant with increasing depth up to 100nm. It was demonstrated that the multilayer film is useful for the depth profiling as a reference material due to its sharp interface features.

REFERENCES

[1] I.L.M Terman, Appl. Surf. Sci. 117/118, 1 (1997)
[2] C.P. Hunt and M.P.Seah, Surf. Interface Anal. 5, 199 (1983)
[3] NIST SRM2531-2536
[4] J. Fine and B. Navinsek, J. Vac. Sci. Tech. A3, 1408 (1985)
[5] K. Kajiwara and R. Shimizu, J. Vac. Sci. Tech. A 13, 1316 (1995)
[6] N. Fukumoto, T. Fujimoto, B. Li, I. Kojima and H. Takaya, J. Surf. Anal. 4, 414 (1998)
[7] cc/min at the standard condition (1 atm, 0°C)
[8] I. Kojima, B.Q. Li, T. Fujimoto, K.J. Kim and D.W. Moon, J. Phys. D:30 , 2143 (1997)
[9] I. Kojima, S. Wei, B.Q. Li and T. Fujimoto, J. Surf. Anal. 4, 70 (1998)
[10] S. Wei, B.Q. Li, T. Fujimoto and I. Kojima, Phys. Rev. B., 58, 3605 (1988)
[11] To be published.
[12] S. Hofmann, Surf. Interface Anal. 21, 673 (1994)
[13] Y. Morita and H. Tokumoto, Appl. Phys. Lett. 67, 2654 (1995)
[14]S. Tanuma, C.J. Powell and D.R. Penn, Surf. Interface Anal., 11, 577 (1988)