Extended Abstracts of the 1993 International Conference on Solid State Devices and Materials, Makuhari, 1993, pp. 636-638

Characterization the Interfacial Layer of N_2O Oxide by Using Ellipsometer and FTIR

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The properties of the oxide films grown by pure N_2O were studied in this work. A two-layer model, considering a N_2O oxide with an oxy-nitride film at the interface, was used to describe the dependence of the main peak shift in a fourier transform infrared (FTIR) spectrum on N_2O thicknesses. The thickness of interfacial layer was determined by FTIR and multiple-angle incident ellipsometer. Both methods showed consistent results and the thickness of this layer is found to be 14-16Å.

1. INTRODUCTION

It has been known that gate oxide grown either in dry O2 then followed by a N2O anneal or in pure N2O is superior in quality to conventional dry oxides [1]. Such a quality improvement is believed to result from piling up of a nitrogen-rich layer at the SiO2/Si interface, which reduces the strain between Si and SiO2. This nitrogen-rich layer is different from that of nitridation of oxide in NH3 ambient. In the case of the latter, nitrogen-rich layers were observed at both interface and top surface of oxide[2]. It has been reported by many researchers that oxide nitrided in NH3 has Si-H bonds as well as O-H bonds, resulting from the H atom of NH3. In contrast, oxide grown with pure N2O owns no Si-H and O-H bonds. Instead, some new Si-N bonds were observed. These Si-N bonds are stronger than Si-H or O-H bonds. Hence, N2O oxide has better hot electron immunity, lower charges trapping, higher breakdown voltage, and better radiation handedness[3]. Many researchers have demonstrated the excellent electrical characteristics of N2O oxide and predicted it as a new gate oxide material for applications in the deep sub-micron ultra-large-scale integrated (ULSI) devices. In this paper, oxides grown in pure N2O at 1 atm were studied by Fourier Transform Infrared (FTIR) spectrum and ellipsometer. From the calculated result, we found the thickness of the interfacial layer is approximately 14-16Å which is consistent with that measured by an ellipsometer.

2. EXPERIMENTAL PROCEDURES

In this work, 4-inch (100) silicon wafers were used as the substrate material. Prior to N2O oxidation process, wafers were subjected to a standard RCA clean followed by a HF:H2O (1:50) dip. Subsequently, wafers were placed into a resistive-heated type furnace and oxidized in a pure N2O ambient at 900-1100°C for 30 to 240 minutes. The thicknesses of oxides were measured by a multiple-angle incident ellipsometer[4]. FTIR was also used to measure the absorbance of various oxides.

3. RESULTS and DISCUSSION

Fig.1 shows the FTIR spectra of five samples. For samples oxidized in N2O at 900°C, 1000°C, and 1100°C for 30 minutes, the peak locations of Si-O are at 1044, 1044, and 1052 cm^{-1}, respectively. All these wave numbers shift significantly from 1070 cm^{-1} of Si-O bond. Thinner oxide has a larger shift. This is mainly due to increase of Si-O intensity with oxide thickness and reduction of the nitrogen replacement percentage in the film grown at higher temperatures. For the films oxidized at a same temperature, in this case of 1000°C, with different oxidation time of 30 (sample b), 120, and 240 (sample a) minutes, the main peak are 1044, 1058, and 1064 cm^{-1} respectively. This trend is the same for the samples with different growth temperature and the same growth time, as mentioned above. Fig.2 shows a comparison of the main Si-O peak for conventional dry O2[5] and N2O oxide grown at 1000°C. For bare Si-substrate, the main peak is at 1100 cm^{-1}. In case of oxide films grown in dry O2, the location of main peak is independent of the thickness of oxide and always locates at 1070cm^{-1}. However, for oxide films grown in N2O, the location changes significantly with thicknesses. The peak shifts from 1044 cm^{-1} to 1064

Table 1 The thicknesses for each layer measured by ellipsometer and FTIR spectroscopy.

	sample a			sample b		
	1-layer	2-layer	total T(Å)	1-layer	2-layer	total T(Å)
Ellipsometer	224	14	238	49	14	63
FTIR	223.5	16.5	240	50.6	14.4	65

cm^{-1} as oxide thickness increases from 63 to 238Å. This implies that the ratio of Si-N bonds to Si-O bonds decreased with increased oxide thickness. From the figure, if the thickness of oxide grown in N2O is beyond 500Å, the main Si-O peak will approach to 1070 cm^{-1}.

Fig.3 shows the proposed two-layer model. In this model, an oxy-nitride layer exists between top oxide and Si-substrate. It has been shown that the amount of peak shift in a FTIR spectrum is a linear function of x for SiO_x [6]. According to this relation, we found the x of sample a which oxidized at 1000°C for 240-minute (thickness 240Å with Si-O peak at 1064 cm^{-1}) and of sample b which oxidized at 1000°C for 30-minute (thickness 65Å with Si-O peak at 1044 cm^{-1}) are 1.9 and 1.6, respectively. Assuming the sandwiched structure is $(SiO_2)_{1-i}(Si_2ON_2)_i$, then its constitution is $Si_{1+i}O_{2-i}N_{2i}$. Therefore, for x= 1.6, i equals 0.154. Likewise, i equals 0.035 for x=1.9. Consequently, the effective compositions for these two-layer structures are calculated to be $SiO_{1.9}N_{0.07}$ and $SiO_{1.6}N_{0.27}$ for sample a and sample b, respectively. For these two compositions, total N atoms in the films were 9.4% for sample b and 2.3% for sample a. All these samples contain a N atomic ratio less than 10%. This implies that these films on the Si-substrate remain to be an oxy-nitrided structure with zero stress[7]. The structural unit for Si2ON2 and SiO2 are SiN3O and SiO4 respectively. Both SiN3O and SiO4 are of tetrahedral structure. For a structure consisting of both SiO4 and SiN3O, atomic ratio of N and O is 3/8. For sample b, the compositional ratio x in $SiO_{1.6}N_{0.27}$ is actually calculated to be 0.25 according to (3/8)x = 0.27/2.87. Similarly, the calculated x value for sample a is 0.06. For these values of x, the Si2ON2 interfacial thicknesses of 16.5 and 14.4Å for sample a and b, respectively, were obtained. Fig.4(a) and (b) show the measured ellipsometric angles of Δ and ψ for sample a and b vs. different incident angles. The measured data (dotted points) fit the simulated data (solid lines) very well. We used the proposed two-layer structure with fixed refractive index 1.46 and 1.77 for the SiO2 layer and Si2ON2 layer[7] in the simulation to obtain the best fitted thicknesses with the least fitting error. The thicknesses for each layer are shown in Table 1. The thicknesses measured by ellipsometer is consistent with that obtained from FTIR.

4. CONCLUSION

In this work, the FTIR spectrum of oxide grown in pure N2O was studied. A two-layer model assuming N2O oxide with a oxy-nitride film at the interface, was used to explain the shift of main peak of Si-O bonds with thicknesses. The thickness of this interface layer was measured by FTIR and ellipsometer. We found the result was consistent. Thickness of this layer was determined to be 14-16Å.

ACKNOWLEDGEMENTS:

This work is supported by National Science Council of China through the contract of NSC-82-0404-1009-190. Authors would like to thank Dr. P. J. Wang for his help of reviewing, also thank Mr. H. H. Chang for FTIR measurement.

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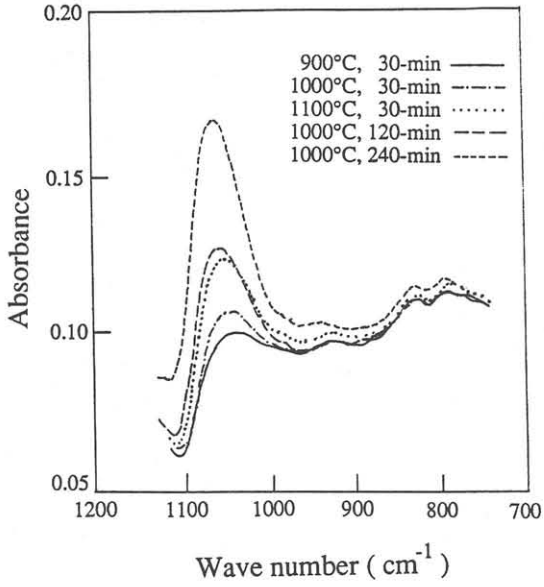

Fig.1 FTIR spectrum for five samples of N2O oxide oxidized at 900-1100°C for 30-240 minutes.

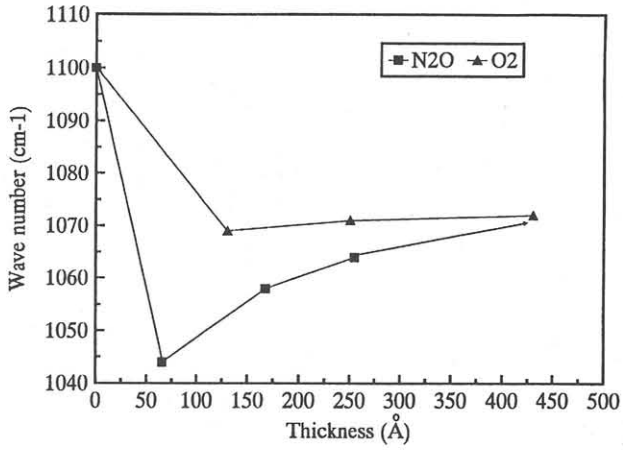

Fig.2 The wave number of Si-O bonds for O2 and N2O oxide vs. thicknesses.

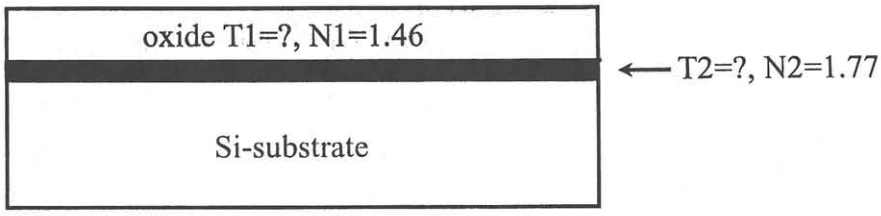

Fig.3 Two-layer model for oxide grown in N2O.

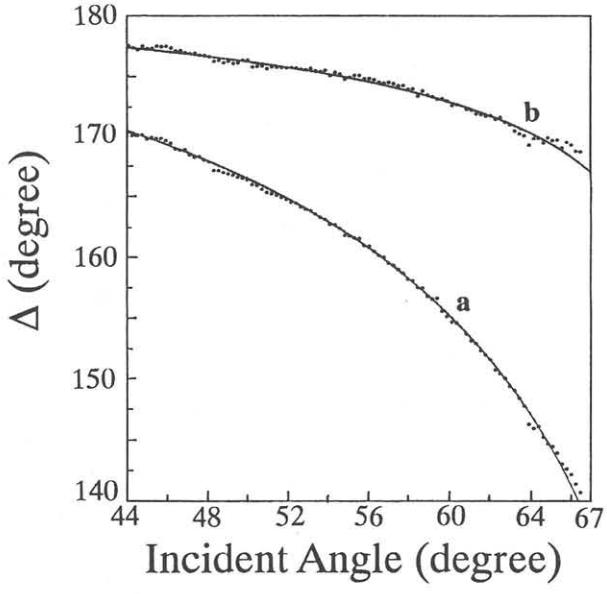

Fig.4(a) Ellipsometric angle Δ vs. different incident angles for N2O oxides with thicknesses 63 and 238Å for sample b and a respectively. Dotted points are measured data and solid lines are the best fitted simulated data.

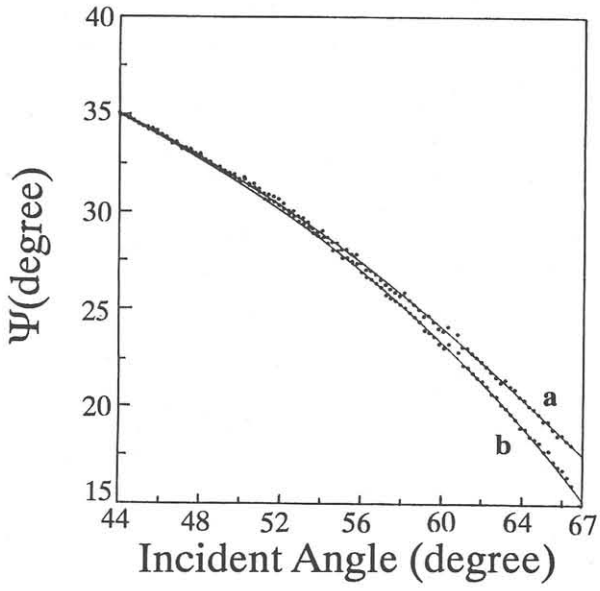

Fig.4(b) Ellipsometric angle ψ vs. different incident angles for N2O oxides with thicknesses 63 and 238Å for sample b and a respectively. Dotted points are measured data and solid lines are the best fitted simulated data.