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P3-3

High Quality Silicon Oxide Film Formed by Diffusion Region PECVD and Oxygen Radical Treatment using Microwave-Excited High-Density Plasma

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1. Introduction

A high quality SiO_2 film formatted by a PECVD technique in which process gases are introduced to the low-electron-temperature diffusion region of a microwave -excited high density plasma and by a oxygen radical post-treatment using a Kr/O_2 microwave-excited high density plasma at 400°C have been developed. The SiO_2 film has good electrical characteristics such as a low leakage current and a high breakdown voltage compared with that of high temperature thermal SiO_2 film.

2. Experimental Method

The experimental equipment, as shown in Fig.1, is capable of generating high-density ($>10^{12}cm^{-3}$) Kr gas plasma by 8.3GHz microwave with a radial line slot antenna (RLSA)[1]. SiH_4 gas were introduced to the diffusion plasma region with low electron temperature (<1eV) for suppressing excess decomposition of SiH_4 and some undesirable gas phase reactions.

After the SiO_2 film deposited, an in-situ oxygen radical post-treatment using Kr/O_2 plasma[2] is carried out. The substrates were n-type (100) crystal silicon or polysilicon. The substrate temperature, microwave power density and pressure are 400°C, 4W/cm^2, and 1Torr, respectively.

3. Results and Discussions

The 1MHz C-V characteristic of the post-treatment and untreated samples is shown in Fig.2. The hysteresis of C-V is observed in the untreated sample. Moreover, the C-V curve of the untreated sample shifts towards positive after gate voltage ramp from positive voltage to negative voltage. It implies that the net negative charges, which come from electrons injected from the substrate into oxide film, are trapped in SiO_2 film. The fixed positive charge densities calculated from V_{FB} shift of the C-V curve are $2x10^{11}cm^{-2}$ for untreated sample and $4x10^{10}cm^{-2}$ for post-treatment sample. The J-E properties of the samples are measured, as shown in Fig.3. It is noticed that J-E curve of the sample untreated moves towards the high field comparing with that of F-N theoretical calculation and that the treated sample is consistent with that of theoretical calculation. Because F-N model is only suite to the samples that exist very low trap density, we can include that the post-treatment by Kr/O_2 plasma can eliminate bulk traps. The decrement of trap density means that the bonding structure and the composition of the film are changed by the post-treatment. The electron traps, in particular for PECVD SiO_2 film, are shown to relate to hydroxyl groups. The characteristic of the bonding groups of the films has been analyzed by FTIR transmission spectroscopy, shown in Fig.4. The result of FTIR indicates that Si-H and Si-OH group density are below the detection limit of FTIR in the PECVD SiO_2 deposited in the study. As known, Si-O, Si-H and Si-OH bonds energy are 6.4eV, 3eV and 2eV, respectively. The average ion energy, however, is only about 3eV in the plasma system. As a result, the ions are not enough to break bonds of Si-O, but enough to break bonds of Si-H and Si-OH and thus, the Si atoms losing OH or H tend to be efficiently bonded by the strongly electronegative oxygen atoms, which the experimental results have demonstrated that Kr/O_2 plasma is capable of producing more efficiently oxygen radicals, leading to inhibited the bonds of Si-H and Si-OH. The J-E characteristic and constant current stress method provides the cumulative breakdown and Q_{bd} distributions of the SiO_2 film deposited and are shown in Fig.6. It can be seen that the breakdown strength of the films is higher than 12MV/cm and the charge-to-breakdown is the same as that of thermal SiO_2 film. The properties of PECVD SiO_2 film comparison with that of thermal SiO_2 film are summarized in table1. The etching rate of 5.7nm/min is a factor of two higher than thermal SiO_2 film. The results suggest that the densification SiO_2 film is deposited on crystalline silicon.

As we know, high quality SiO_2 film deposited on polysilicon at low temperature is important for the applications. Fig.6 shows the J-E characteristics of thermal (1000°C, dry oxidation) and PECVD (400 °C) polyoxide films. It is observed that localized breakdown occurs in the thermal polyoxide and after the first soft breakdown polyoxide is still intact, but exhibits a high leakage current at low field strength. However, PECVD polyoxide exhibits low leakage current at blow 6MV/cm.

4. Conclusions

The high quality SiO_2 film compared with a high temperature thermal SiO_2 film have been achieved by the PECVD technique in which process gases are introduced to the low-electron-temperature diffusion region of a microwave-excited high density plasma and by the oxygen radical post-treatment using a Kr/O_2 microwave-excited high density plasma at 400°C. The experimental results demonstrate that bulk trap density attributed to be Si-OH is greatly decreased with the oxygen radical post-treatment by Kr/O_2 plasma. This high quality PECVD SiO_2 film can apply to many low-temperature processing's such as a TFT gate insulator and flash memory inter-poly film.

References

[1] M. Hirayama et al, in Ex. Abst. of the 43rd National Sym. of American Vac. Soc., Philadelephia (1996) p.134.

[2] T. Ohmi et al, The 199th Mtg. of the Electrochemical Soc. Abst. No.270, Vol.2001-I, Washington, DC (2001)

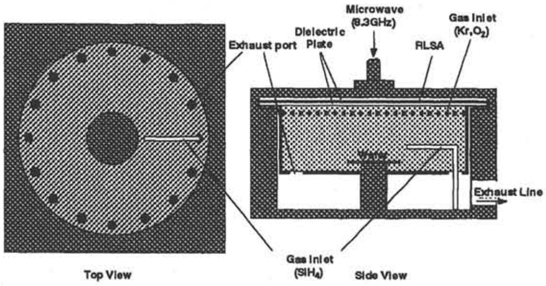

Fig.1 A schematic of the high density low energy plasma system

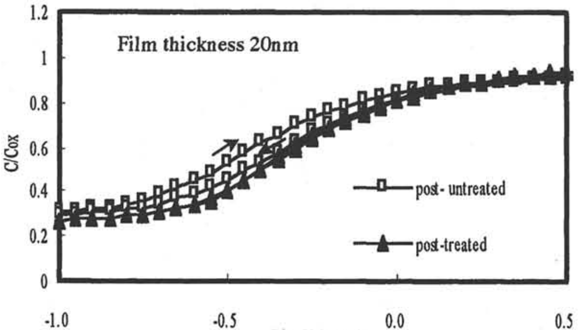

Fig.2 Effect of post-treatment on the C-V property
There is no hysteresis with the treatment.

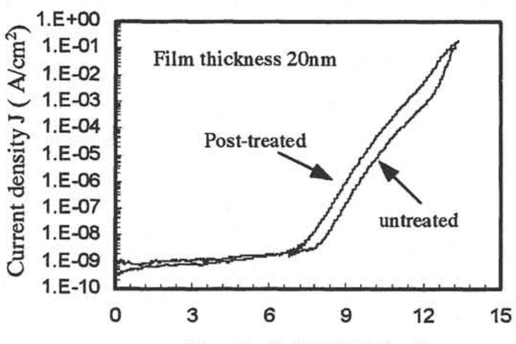

Fig.3 Effect of post-treatment on the J-V property

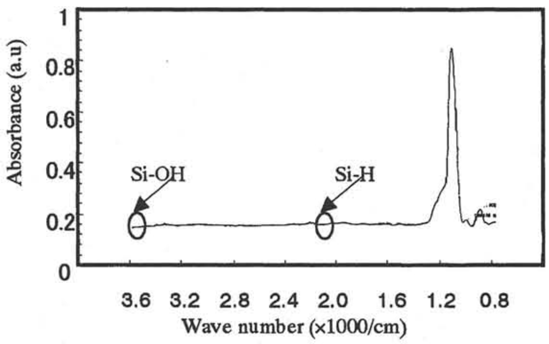

Fig.4 FTIR spectrum of the PECVD SiO_2 film
The peak of Si-OH and Si-H is not observed.

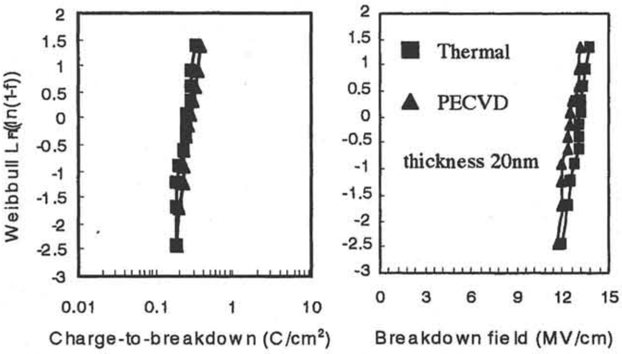

Fig.5 Breakdown field and Q_{bd} comparison with that of thermal silicon oxide (dry oxidation, 1000°C)
The breakdown properties of the PECVD SiO_2 film is the same as that of thermal SiO_2 film.

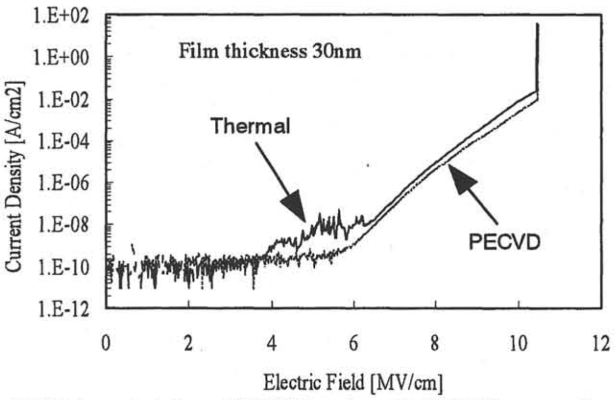

Fig.6 J-V characteristics of PECVD polyoxide (400°C) comparison with that of thermal polyoxide (dry oxidation, 1000°C)

Table1 Properties of the PECVD SiO_2 film in the study

	PECVD SiO_2	Thermal SiO_2
Refractive Index	1.46	1.46
O/Si atom ratio (XPS)	2.0	2.0
Etch rate (0.5%HF, 25°C) (nm/min)	5.7	2.7
Fixed Charge Density (cm^{-2})	4x10^{10}	2x10^{10}
Breakdown Strength (MV/cm)	> 12	>13
Interface State Density Dit (eV^{-1}cm^{-2})	1.5x10^{11}	10^{10}