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SILICON OXIDE FILMS PREPARED BY PLASMA OXIDATION OF SILICON AND THEIR APPLICATION FOR TUNNEL MIS DIODES[1]

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Silicon oxide films in the thickness range of 1—4 nm have been prepared by oxidation of silicon in oxygen plasma. The film thickness was measured by ellipsometry with $\lambda = 632.8$ nm. The properties of MIS tunnel diodes have been determined from I—V and C—V characteristics.

I. INTRODUCTION

Very thin silicon dioxide films in the range of 1.5—10 nm, are being investigated for applications in several types of silicon devices. These thin oxides are usually prepared by oxidation of silicon in oxygen or steam at temperatures of 400—1000 °C [1], [2]. Alternative methods for the oxidation of silicon to produce very thin films, as the steam of boiling water, boiling water, room temperature air [3] DC plasma oxidation [4] have been used. The very thin oxides described in this paper have been prepared by low temperature oxidation in RF oxygen plasma [5]. Plasma oxidationof Si is very interesing for semiconductor processing technology. Very thin oxides have been characterized by ellipsometry, infrared spectroscopy, and Auger electron spectroscopy. The results tend to support the concentration of a very thin interfacial silicon rich SiO_x region with a maximum thickness of 2.5 nm.

In order to exploit the possibility of using RF oxygen plasma to grow ultrathin oxide on silicon, the characteristics of the MIS tunnel diodes versus the technological conditions of preparing a tunnelling oxide, have been analysed. The present study consists of measurements of the I—V and C—V characteristics of such diodes.

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Experimental details

The process of plasma oxidation and the preparation of the MIS diodes was carried out in a vacuum system schematically presented in Fig. 1.

The RF electrode was connected with the power 13.56 MHz generator trough a matching network. Oxygen was introduced into the chamber through a mass flow controller. Argon, hydrogen and nitrogen were introduced into the chamber through needle valves. Prior to the plasma oxidation n-type silicon wafers of 63 mm in diameter with a resistivity of 2—5 Ωcm and (100) orientation were standard cleaned and then etched in dilute hydrofluoric acid, rinsed in deionized water and dried. After having been loaded into the chamber on the RF electrode, the vacuum system was evacuated to a 10^{-3} Pa pressure. During the plasma oxidation parameters such as temperature, pressure, time of oxidation were changed. The MIS diodes were made on (100) 76 mm in diameter 500 μm thick n-type Si wafers with a resistivity of 2—5 Ωcm. After a standard cleaning a thick Al layer of 1 μm was evaporated on the back side of the wafers, using electron beam evaporation. Before making the MIS contact, the wafers were etched for 20 s in dilute hydrofluoric acid. The parameters of the technological steps such as argon plasma cleaning before oxidation, hydrogen annealing before and after oxidation and other parameters such as oxidation time were changed. This was followed by the evaporation of a 200 nm thick Au layer on the front side of the wafer by using the W-boat. Then a layer of photoresist was placed on the fronts and the backs of the wafers, the wafers were exposed through photolitographic mask and then etched to obtain diodes with the front electrode diameter of 0.7 mm.

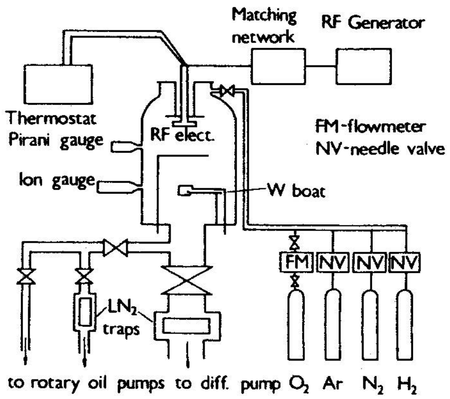

Fig. 1. Schematic diagram of the system used for RF plasma oxidation and the preparing of MIS diodes.

II. RESULTS AND DISCUSSION

The oxidation rate and the refractory index of plasma oxide were measured by the ellipsometer LEM 2 at the angle of incidence of 70.00° and the wavelength of 632.8 nm. In Fig. 2 there are shown the dependence of film thickness versus oxidation time with the parameters temperature and pressure. Fig. 2 shows that the oxidation rates of the 1, 2, 3, 4 type technological processes depend mainly on the temperature of oxidation, while the influence of pressure is small. The kinetics of oxidation is not different. The growth of the layer in oxygen plasma is controlled in the initial phase by the linear-parabolic law [2]. After 30 s of oxidation the growth of the layer decreases, but the linear-parabolic law remains. The change of the oxidation rate is not known. A similar shape has the oxidation curve in [6], where the oxidation was carried out in microwave oxygen plasma.

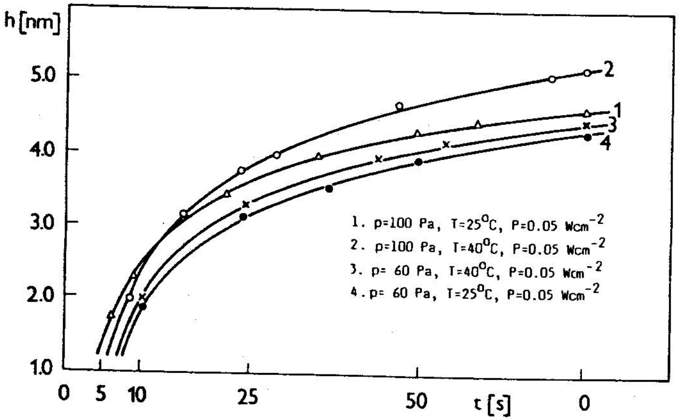

Fig. 2. Film thickness vs oxidation time.

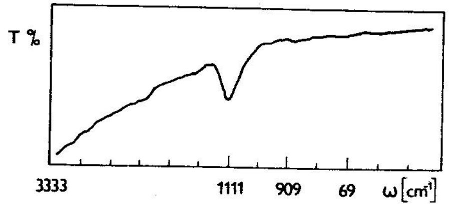

Fig. 3. The *IR* transmission spectra of a thin plasma oxide film.

We assume that plasma oxidation is a process limited by the difusion of the oxidation particles through the growing oxide. The refractive index of these films was approximately 1.55. This is more than the value of the bulk oxide refractive index, but the value 1.55 is in agreement with [2].

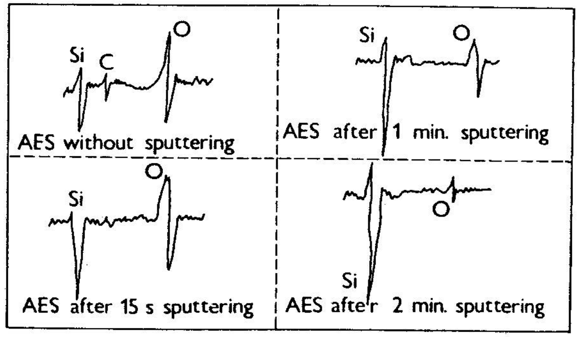

Fig. 4. AES spectra of plasma oxide vs time of sputtering.

In Fig. 3 the *IR* transmission spectrum of the plasma oxide is shown. The spectra were measured by the two beam compensating method. There was no difference between the *IR* spectra of the 1, 2, 3, 4 samples when we used samples with a uniform thickness of the plasma oxide. In all cases the absorption maximum in the *IR* transmission spectra was $\lambda = 1100\,\mathrm{cm}^{-1}$, which is responsible for the Si—O bond. The composition of the plasma oxide was analysed by AES. AES spectra versus sputtering time are in Fig. 4. On the spectrum without sputtering silicon, carbon and oxygen are shown. After 15 seconds of sputtering the peak of the carbon is not present in the AES spectrum. This can be explained by the carbon being present only on the surface of the oxide layer. After 30 seconds or 1 minute of sputtering the oxygen peak amplitude decreases and after 2 minutes of sputtering the oxygen peak disappears. We conclude that the concentration of oxygen drops to the interface SiO_2—Si, while the concentration of silicon is constant. It is evident that silicon is in the atomic and bonding state of the plasma oxide layer. Only the presence of oxygen, silicon and carbon (at the beginning of sputtering) in the AES spectra are shown, but on the other hand in the optical emission spectrum of oxygen plasma (Fig. 5) the Ar, Fe and N_2 are present. This can be explained by very small concentrations of the Ar, Fe and N_2 in the oxide layer. They may be under the detection limit of the AES.

In the next part of the paper we are going to analyse the influence of the preparation conditions of the tunnel oxide on the *I*—*V* and *C*—*V* characteristics of the tunnel MIS diodes.

The influence of the oxidation time on the I—V characteristics of the diodes A, B, C, D is shown in Fig. 6. The oxidation times were: A = 30 s, B = 45 s, C = 60 s, D = 5 s and the parameters of the oxidation process were (P = 100 Pa, T = 40 °C, P = 0,05 W cm^{-2}). The reverse and the forward currents of the diodes decreased with increasing oxidation time. This can be explained by the increase of the thickness of the oxide l ayer with oxidation time and then the decrease of the tunnelling current through the thin oxide layer. The ideality factors are: $n_A = 2.12$, $n_B = 2.468$, $n_C = 2.695$, $n_D = 2.809$. In Fig. 7 the I—V characteristics of the linear scale are shown. The distinctive feature in this region is the plateau in curve B, C, D near zero bias. This corresponds to the semiconductor surface being depleted [7]. The C—V characteristics of the diodes A, B, C, D are shown in Fig. 8.

We have also computed the barrier height from the I—V and C—V characteristics of the diodes A, B, C, D. The values of the barrier height are in Table 1.

The I—V characteristics of the diodes H, K, L that were oxidized in oxygen plasma (100 Pa, 0.05 W cm^{-2}, 40 °C, 40 s) and those cleaned in the Ar plasma before oxidation (1 Pa, H = 100 V self bias V sb, K = 200 V sb, L = 300 V sb, 1 min) are shown in Fig. 9. With an increasing DC self bias of the Ar plasma,

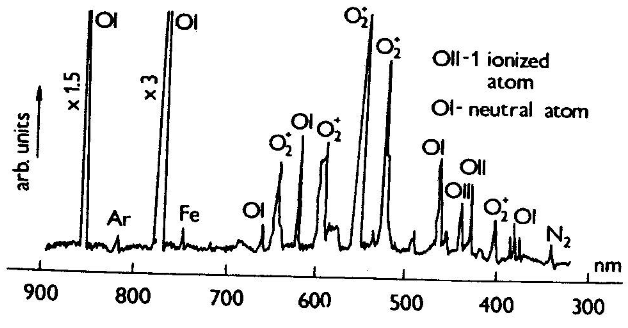

Fig. 5. Optical emission spectrum of the oxygen plasma.

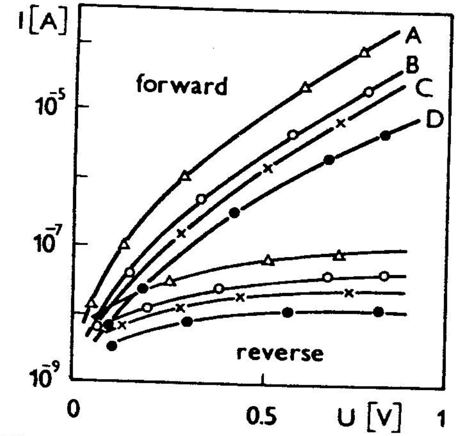

Fig. 6. I—Vcharacteristics of diodes A, B, C, D.

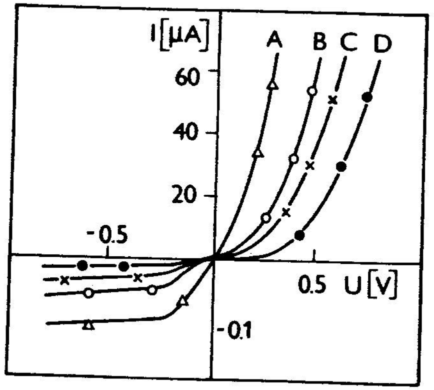

Fig. 7. I—V characteristics of diodes A, B, C, D in linear scale.

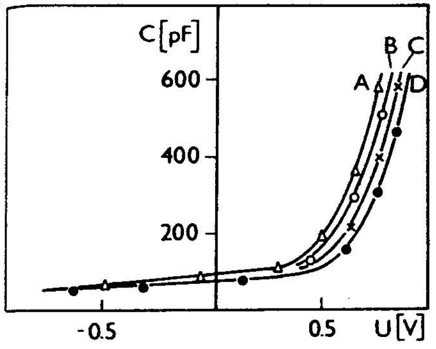

Fig. 8. C—V characteristics of diodes A, B, C, D.

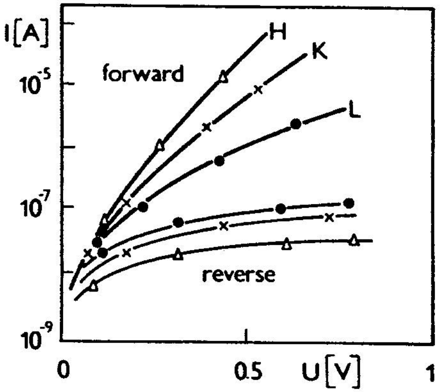

Fig. 9. I—V characteristics of diodes H, K, L.

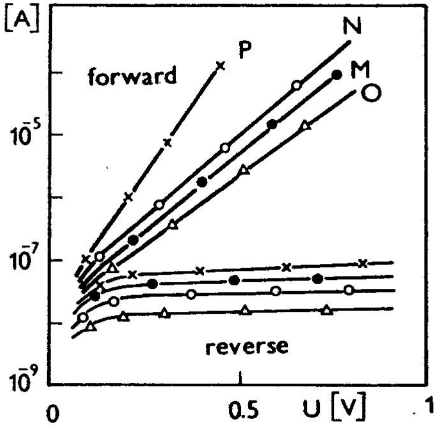

Fig. 10. I—Vcharacteristics of diodes M, N, O, P.

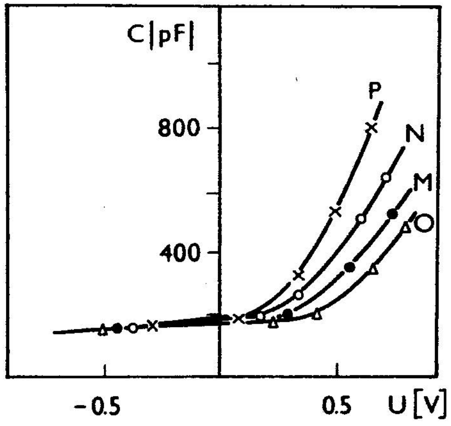

Fig. 11. C—V characteristics of diodes M, N, O, P.

the increase *reverse* current of the diodes and the increase ideality factors are: $n_N = 1.634$, $n_K = 1.869$, $n_L = 2.33$. This can be explained by the Ar ion of higher energy disturbing the Si bonds on the surface, which results in the increasing interface state density.

Table 1
Barrier heights of diodes A, B, C, D

	Θ_B (*C—V*)	Θ_B (*I—V*)
A	0.750	0.698
B	0.695	0.769
C	0.892	0.775
D	0.780	0.785

The *I—V* characteristics of the diodes M, N, O, P that were M-annealed (H_2, 200 Pa, 200 °C, 10 min) after oxidation (O_2, 100 Pa, 0.05 W cm^{-2}, 40 °C, 40 s), N-annealing before oxidation after cleaning in the Ar plasma (1 Pa, 100 V self bias, 1 min) O-annealed before and after oxidation, P-annealed before oxidation, are shown in Fig. 10. The ideality factors of the diodes are: $n_M = 2.59$, $n_M = 2.28$, $n_O = 2.88$, $n_p = 1.56$. Since both the thickness of the oxide layer and the interface state density influence the ideality factor, we can conclude that annealing in H_2 is suitable before cleaning and after oxidation. The influence of annealing before cleaning and after oxidation. The influence of annealing before cleaning is not well understood. When we have used annealing before and after oxidation, it is possible to increase the thickness of the thin oxide results in the increase of the ideality factor. The difference between the *I—V* characteristics of the diodes M and N is degligible. In Fig. 11 are shown the *C—V* characteristics of the diodes M, N, O, P. In this case, we did not compute the barrier heights of the diodes.

III. CONCLUSION

Silicon samples have been oxidized by low temperature oxygen plama to obtain films 1.5—4 nm thick. The growth of the oxide in low pressure low temperature oxygen plasma follows the linear-parabolic law. The very thin oxides have been characterized by infrared spectroscopy, the Auger spectroscopy and elipsometry. No impurities were detected within the films. The height of the film refractive index is 1.55. This high value may be caused by the thin interfacial layer with refractive index 2. The *I—V* and *C—V* characteristics of the tunnel MIS diodes are similar to those of the minority carrier MIS tunnel diodes in [4]. The ideality factor appears to be highly dependent on the oxide thickness and the preparation conditions of the tunnel barrier. Although having similar properties, the minority carrier MIS tunnel diode has a distinct advantage over the *p-n* junction diode in is easy fabrication. In addition to having applications as injecting contact, as photodiode, the device is well suited to direct energy conversion by means of the electron or photovoltaic effect.

REFERENCES

[1] Fehlner, F. P.: J. Electrochem. Soc., *23* (1982), 119.
[2] Adams, A. C., Smith, T. E., Chang, C. C.: J. Electrochem. Soc., *8* (1980), 12.
[3] Raider, S. I., Flitsch, R., Palmar, M. J.: J. Electrochem. Soc., *413* (1985), 122.
[4] Beck, R. B., Ruzyllo, J.: Thin Solid Films, *13* (1986), 136.
[5] Guldan, A., Huran, J., Čupcová, L.: Electrotechn. čas., *36* (1985), 90.
[6] Kimura, S. I.: J. Electrochem. Soc., *135* (1985), 1460.
[7] Shewhun, J., Green, M. A, King, F. D.: Solid-State Electronics, *1* (1984), 563.

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ТОНКОПЛЕНО4НЫЕ ОКИСИ КРЕМНИЯ ИЗГОТОВЛЕНЫ ПЛАЗМЕННЫМ ОКИСЛЕНИЕМ И ИХ ПРИМЕНЕНИЕ ДЛЯ ТУНЕЛЬНЫХ МДП ДИОДОВ

Были изучены свойства тонких пленококиси кремния изготовленные окислением кремния в кислородной плазме. Толщина пленок была измерена элипсометром (λ = 632,8 нм) в диапазоне 1—4 нм. Свойства МДП тунельных диодов были определены из I—V, C—V зависимостей.