Properties of atmospheric pressure plasma oxidized layers on silicon wafers

Abstract: In this research a new process of plasma oxidation of crystalline silicon at room temperature is studied. The plasma oxidation was carried out using Diffuse Coplanar Surface Barrier Discharge (DCSBD) operating in ambient air and oxygen at atmospheric pressure. The influence of exposition time, plasma parameters and crystallographic orientation of silicon on oxidized layers and their dielectric properties were investigated. Thickness, structure and morphology of these layers were studied by ellipsometry, infrared absorption spectroscopy and scanning electron microscopy. During the treatment time, from 1 to 30 minutes, oxidized layers were obtained with thickness from 1 to 10 nm. Their roughness depends on the crystallographic orientation of silicon surface and exposure time. Electrical parameters of the prepared layers indicate the presence of an intermediate layer between silicon substrate and the oxidized layer.

Keywords: Amorphous silicon oxide, atmospheric pressure plasma, oxidation, DCSBD

DOI: 10.1515/chem-2015-0047
received January 31, 2014; accepted May 8, 2014.

1 Introduction

Properties of the surface/interface silicon based layers play an important role in semiconductor industry. Different applications need various behaviors of these surface/interface layers. However the modification of the surface properties of the silicon based layer is often toxic or high energy consuming [1-3]. Recently, there is a tendency to replace these non-ecological processes by methods using plasma technology, which often provides an environmentally acceptable alternative. Although, the low pressure plasma technology is more efficient and already commonly used in industry, there is a tendency to replace it by atmospheric pressure plasma technology. Recently, various atmospheric pressure plasma sources have been received increasing interest due to their many advantages and are increasingly used in industry. The most important advantage of atmospheric pressure plasma sources is their easy utilization and the absence of vacuum techniques resulting in faster, easier manipulation and in-line processes [4-7].

In our previous article [8] we discussed an oxidation process of Si (111) using atmospheric pressure plasma generated by Diffuse Coplanar Surface Barrier Discharge (DCSBD). DCSBD represents dielectric barrier discharge in coplanar geometry operating at atmospheric pressure. Due to the geometry, DCSBD produces a large area of thin layer of non-equilibrium cold plasma on the surface of the dielectric barrier with high density of active particles [9-11]. Such geometry and properties provide many options for fast discharge surface modification (e.g. cleaning, activation) of various materials, especially for large flat surfaces such as wood, nonwoven textile, glass etc [12-15].

In this research, we have studied the effect of the Si surface orientation and working gas on the oxidation process and as well, the properties of produced layers. The plasma oxidation was carried out using DCSBD operating at atmospheric pressure in ambient air and oxygen, respectively. The oxidation of Si surface with crystallographic orientation (111) and (100) was compared, the effect of native oxide was discussed and also the dielectric properties of oxidized layers were measured. It was found that oxidation of Si surface in DCSBD at room temperature at a process time of few minutes produces...
homogenous thin oxide layer with the thickness of nanometres. The influence of exposition time, substrate pre-treatment, crystallographic orientation of silicon on oxidized layers on their properties was investigated.

2 Experimental Procedure

The plasma was generated at atmospheric pressure by DCSBD. The DCSBD geometry consists of many parallel silver electrodes embedded in Al₂O₃ ceramics, see Fig. 1 [10,11]. The discharge was powered by a high frequency voltage (14 kHz, 13 kV peak to peak, 300 W). The distance between the sample and the ceramics plate was 0.3 mm. The treatment has been carried out in ambient air or oxygen at various treatment times. In the case of air treatment, the chamber was opened and the plasma was generated in ambient air, at room temperature, in case of oxygen atmosphere, the chamber was under flow regime with oxygen Q[O₂] = 1 l min⁻¹ with purity of 99.999%.

Two types of one-side polished Si substrates have been used: n- type, doped with phosphorous, Si (111) having resistivity (7 -13)10⁻³ Ω cm and p-type, doped with boron Si (100) having resistivity (6-12)10⁻³ Ω cm purchased from ON Semiconductor, Czech Republic. The thickness of the substrates was 525±38 μm. Before plasma treatment all samples were cleaned by isopropyl alcohol, dried by flow of air. One series of samples were then immersed in 1% HF solution at room temperature for 45 s for native oxide removal and last dried by flow of air. In this case the surface silicon atoms tend to be hydrogen terminated.

The oxide films that formed on the Si surface were analyzed by spectroscopic ellipsometer (S2000, Rudolph Research) with the fixed incidence angle of 70°. The ellipsometric angles Psi and Delta were measured in the wavelength range from 280 to 800 nm. The single layer Cauchy dispersion model has been used to estimate the thickness of the oxidized layer.

The molecular structure of the oxidized layers was characterized by Fourier Transform Infrared Absorption Spectroscopy (FT-IRRAS). The vacuum FT-IR spectrometer (BRUKER, VERTEX 80V) with a reflection unit, which allows variations of the incidence angle and the state of polarization, has been used. The sample compartment was evacuated to 2 mbar to reduce the water absorption. The p-polarized IR beam with incidence angle of 68° were determined and the absorbance was measured in the wavenumber range of 4000 cm⁻¹ to 600 cm⁻¹.

The surface morphology of the oxidized Si surface was observed by scanning electron microscopy (TESCAN Mira 3) equipped with a Schottky Field Emission electron gun, secondary electron detector and back-scattered electrons detectors and both detector also located in the objective lens. Maximal resolution is 1.0 nm by 30 kV.

![Figure 1](image.png)

**Figure 1:** The schematic of a) DCSBD reactor and b) cross-section of an electrode system.
Dielectric properties have been measured by LCR Meter for frequency range 100-20000 Hz at different temperatures. In this case, Al contacts (5 mm in diameter) with the thickness of 100 nm were evaporated on the oxide layer after the oxidation process.

3 Results and Discussion

Growth kinetics for oxidation of Si (111) surface in air and oxygen plasma and of Si (100) in air plasma are shown in Fig. 2. The oxidation process is nonlinear and the amount of oxygen did not increase the growth rate. During the treatment time from 1 to 30 minutes, oxidized layers were obtained with a thickness from 6 to 11 nm. Oxide thickness on the surface reaches its maximum after 7 minutes, further oxidation brings the constant thickness to about 10 nm. The oxidation rate at our experimental conditions is comparable to dry thermal oxidation at 900°C [16], low pressure anodization and low pressure microwave plasma.

Very similar results were obtained with both Si (111) and Si (100) substrates; the plane (111) has the highest area density and lowest surface energy, while the plane (100) has the highest surface energy and the lowest atomic density. On the contrary, experiments show that the native oxide layer on silicon is growing faster on the n-type Si with (111) orientation than on the p-type silicon with (100) orientation [17].

The structure of these layers was studied by SEM. When rocking the primary electron beam, backscattered electrons create so called electron channelling patterns (ECP). The ECP obtained for clean and oxidized surface at accelerating voltage 30.0 kV and 3.0 kV are illustrated in Fig. 3. Clean Si crystalline surface before plasma treatment are represent by strong ECP in all cases. On the other hand, oxidized Si surface is represented by an attenuated ECP with the lowering of the SEM accelerating voltage; i.e. when testing the area closer to the surface. This gives evidence of the existence of an amorphous structure of the surface layer after plasma treatment.

The (001) termination of the Si substrate exposes two dangling bonds per Si atom, which can be saturated by the O atoms forming $\text{Si}^n\text{O}$, $\text{Si}^{n+2}\text{O}_2$, and $\text{Si}^{n+3}\text{O}_3$. This layer shows peculiar electronic, dielectric, and vibrational properties, and affects the carrier flow in the Si channel of CMOS devices. Generally, low temperature oxidation process provides $\text{SiO}_x$ layers with $0 < x < 2$.

Fig. 4. shows IRRAS absorption spectra of the oxide layers prepared after different treatment time for both crystallographic orientation, Si (100) and Si (111), respectively. The spectrum of the blank sample was measured for each sample before plasma treatment and background spectra were measured (before the measurement) and then were automatically subtracted from every spectrum. IR spectra of Si (100) and Si (111) with native oxide and HF pre-cleaned are characterized only by Si-O-Si peak at ~1240 cm$^{-1}$ representing longitudinal optic (LO) mode of Si-O-Si vibration. Absorbance increases with increasing oxide thickness independently on the crystallographic orientation or the presence of the native oxide. Moreover, the maximum of Si-O-Si peak tends to decrease with decreasing oxide thickness.

This frequency shift for ultrathin $\text{SiO}_2$ layer is often explained by the change of the Si-O-Si bond angle due to surface effects or the existence of non-stoichiometric oxide at the $\text{SiO}_2$-Si interface [19]. More realistic models of the $\text{Si-SiO}_2$ interface reflect the disordered nature of the transient part [20]. The average bond length in the substoichiometric oxide is larger than in bulk $\text{SiO}_2$ [21]. In the case of thin $\text{SiO}_2$ layer, this transient part strongly affects the IR spectra. The observed trend in the experimental data (Fig. 4) supports the idea that the origin of LO red shifts resides in the softer vibrational modes of the substoichiometric interfacial layer due to the larger bond length. More pronounced changes are observed when comparing the oxidized layers with HF pre-cleaning to the oxidized layers with native oxide. This indicates that the transient region is thinner with steeper prolongation of the Si-O bonds when the HF pre-cleaning is made. This agrees with the capacitance measurements (see Fig. 4).
Figure 3: Electron channeling pattern at accelerating voltage of a) 30 kV and b) 3 kV: left: untreated sample Si (100); right: 30 min oxygen plasma treated sample Si (100).

Figure 4: a) Si-O-Si peak at ~1240 cm\(^{-1}\) representing LO mode of Si-O-Si vibration of the oxidized layers after various treatment time and conditions b) corresponding peak shift maximum in dependence on the thickness of oxide layer.
The dielectric permittivity is used as a measure of the gate capacitance density in MOS devices via EOT - equivalent oxide thickness. Thus, the accurate determination of the dielectric permittivity at the Si (100)-SiO$_2$ interface is very important. However, a thorough understanding of the dielectric effect of the interfacial layer is still missing to date due to the peculiar structural and electronic properties of that layer. The measured capacitance densities of the samples in frequency range 100-20000 Hz at different temperatures are presented in Fig. 5a, b. When we used a one layer model we obtain a discrepancy between measured and calculated data. According to [6,22,23] we suggest that in our samples a suboxide layer SiO$_x$ is present. Moreover, we cannot bear the thickness from the ellipsometry directly into calculation as ellipsometric measurements probe the optical path of a light beam while the dielectric response is from other frequency range. This is in agreement with the SEM results. Another evidence of this suboxide interlayer is supported by the temperature variation of the frequency dependencies of the capacitance densities for the layer treated with native oxide and with HF pre-cleaning (Fig. 5a, b). Even if the optical thicknesses are practically the same the capacitance density is lower for HF pre-cleaned sample. This reveals a different effective thickness and from different temperature behaviour in the low frequency region in the HF pre-cleaned samples the presence of two layers with different types of thermally activated mechanism.

4 Conclusions

In this research a new process of plasma oxidation of crystalline silicon at room temperature was studied. It was found that by means of DCSBD operating under atmospheric pressure in air or oxygen we are able to prepare silicone dioxide layers with maximum thickness of 10 nm and amorphous structure. The thickness of the oxidized layers is independent of the surface crystallographic orientation and the presence of native oxide does not influence the final thickness. Dielectrical measurements of the prepared layers indicate the presence of an intermediate layer between substrate and the oxidized surface layer. The electrical properties could be promising for further applications; however some work elucidating properties of the formed suboxide transient layer must be done.

Acknowledgements: This work was supported by the project “R&D Centre for low-cost plasma and nanotechnology surface modifications” was created at the Masaryk University in the Operational Programme Research and Development for Innovation, Reg No. CZ.1.05/2.1.00/03.0086.

References

[1] Sifert P., Krimmel E., Silicon: evolution and future of a technology, Springer - Verlag, New York, 2004, pp. 22.
[2] Kasap S., Capper P., Springer handbook of electronics and photonic materials, Springer, New York, 2007, pp. 373, 659.
[3] Sze S.M., Kwok K.NG, Physics of Semiconductor Devices, John Wiley and Sons, New Jersey, 2007, pp. 197.
[4] Taylor S., Zhang J.F., Eccleston W., A review of the plasma oxidation of silicon and its applications, Semicond. Sci. Tech., 1993, 8, 1426.
[5] Tinoco J.C., Estrada M., Baez H., Cerdeira A., Room temperature plasma oxidation: A new process for preparation of ultrathin layers of silicon oxide, and high dielectric constant materials, Thin Solid Films, 2006, 496, 546-554.
[6] Giustino F., Pasquarello A., Electronic and dielectric properties of a suboxide interlayer at the silicon-oxide interface in MOS device, Surf. Sci., 2005, 586, 183-191.

[7] Hess D.W., Plasma-assisted oxidation, anodization, and nitridation of silicon, IBM J. Res. & Dev., 1999, 43, 127-145.

[8] Skácelová D., Danilov V., Schäfer J., Quade A., Sťahel P., Černák M., Meichsner J., Room temperature plasma oxidation in DCSBD: A new method for preparation of silicon dioxide films at atmospheric pressure, Mat. Sci. Engineer: B, 2013, 178, 651.

[9] Černák M., Černáková L., Hudec I., Kováčik D., Zahoranová A., Diffuse Coplanar Surface Barrier Discharge and its applications for in-line processing of low-added-value materials, Eur. Phys. J. Appl. Phys., 2009, 47, 1-6.

[10] Černák M., Method and apparatus for treatment of textile materials, European Patent EP 1387901 B1, 2002.

[11] Černák M., Ráhel J., Apparatus and treatment method of wood surface, wood fibres and wooden. Patent WO 2008085139. 2008.

[12] Šimor M., Ráhel J., Vojtek P., Černák. M., Atmospheric-pressure diffuse coplanar surface discharge for surface treatments, Appl. Phys. Lett., 2002, 81, 2716-2718.

[13] Pamreddy A., Skácelová D., Haničinec M., Sťahel P., Stupavská M., Černák M., Havel J., Plasma cleaning and activation of silicon surface in Dielectric Coplanar Surface Barrier Discharge, Surf. Coat. Technol., 2013, 236, 326-331.

[14] Štepánová V., Skácelová D., Slaviček P., Černák M., Chem. listy, Diffuse coplanar surface barrier discharge for cleaning and activation of glass substrate, 2012, 106, 1495-1498.

[15] Fialová M., Skácelová D., Sťahel P., Černák M., Chem. listy, Improvement of surface properties of reinforcing polypropylene fibres by atmospheric pressure plasma treatment, 2012, 106, 1439-1442.

[16] Deal R.E., Grove A.S., General Relationship for the Thermal Oxidation of Silicon, J. Appl. Phys., 1965, 36, 3770-3778.

[17] Zhang X.G., Electrochemistry of Silicon and Its Oxide, Kluwer Academic/Plenum Publishers, New York, 2001.

[18] Green M.L., Gusev E.P., Degraeve R., Garfunkel E.L., Ultrathin (<4 nm) SiO2 and Si-O-N gate dielectric layers for silicon microelectronics: Understanding the processing, structure, and physical and electrical limits, J. Appl. Phys., 2001, 90, 2057.

[19] Lisovskii I.P., Litovchenko V.G., Lozinskii V.G., Steblovskii G.I., Development of the structure of thin SiO2 films during thermal growth on Si substrate, Thin Solid Films, 1992, 213,164-169.

[20] Diebold A.C., Venables D., Chabal Y., Muller D., Weldon M., Garfunkel E., Characterization and production metrology of thin transistor gate oxide films, Mat. Sci. Semicon. Proc. 2, 1999, 45, 103-147.

[21] Mauri F., Pasquarello A., Pfrommer B.G., Yoon Y., Louie S. G., Si-O-Si bond-angle distribution in vitreous silica from first-principles Si-29 NMR analysis, Phys. Rev. B, 2000, 62, R4786-R4789.

[22] Chang H. S., Yang H.D., Hwang H., Cho H.M., Lee H.J., Moon D.W., Measurement of the physical and electrical thickness of ultrathin gate oxides, J. Vac. Sci. Technol. B, 2002, 20, 1836.

[23] Giustino F., Pasquarello A., Theory of atomic-scale dielectric permittivity at insulator interfaces, Phys. Rev. B, 2005, 71, 144104.