A NEW PROCESS OF OXIDE GROWTH ON SILICON

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ABSTRACT

A new technique of growing silicon dioxide film is described. The film is obtained from a organosilane derivative. The film is evaluated for bond-strain, porosity, etc., by infrared spectroscopy, P-etch, density and refractive index measurements. Though the as-deposited film lacks desirable properties, a very good film can be obtained by densification of the deposited film.

Key words: SiO_2 deposition, organosilane derivative.

INTRODUCTION

High temperature (900° C–1200° C) oxidation of silicon can produce very pure and stable silicon-dioxide films. But high temperature thermal oxidation process suffers from the disadvantage of junction movement and junction degradation [1]; also this process cannot be used for deposition of silicon dioxide on other substrates.

The films of SiO_2 have also been produced by decomposition of ethyl-silanes such as tetraethoxy silane [2] or oxidation of silane [3] but these films suffer from the disadvantages of high porosity, high etch rates and a high load of carbon contamination and less stability towards moisture.

In this article we will describe a new technique of growing oxide and evaluate its physical and chemical properties.

EXPERIMENTAL PROCEDURE

(*a*) *Oxide Deposition*

The oxide film is deposited from a organo-silane compound (acyloxy-silane). The compound is dissolved in a suitable organic solvent (*e.g.*, acetone) and is applied on the wafer which is mounted on a 'Spinner'. The centri-fugal forces distribute the liquid evenly and the excess material is thrown off at the substrate edges. The compound reacts in the air and produces SiO_2 layer almost instantaneously.

Silicon wafers of *n*- and *p*-types of different resistivities and two types of crystal orientation (⟨100⟩ and ⟨111⟩) are used as substrates. No change was found in the deposited film properties (described latter). The surface finish of the substrates is a very important factor. On badly prepared surfaces discontinuous films are produced. All descriptions that will follow are regarding to optical-polish-finished surfaces. The cleaning of the substrates is also an important factor. If the surface is not properly degreased no films could be grown. The wafers are cleaned by the method described in [4].

The thickness of the film is dependent on the spinner speed; with higher speed the thickness reduces as shown in Fig. 1. In general, uniform thicknesses of the film is obtained for spinner speed greater than 3000 rpm. In the 1000–2000 rpm range, two regions of films are obtained as shown in Fig. 1 inset. The region A covered almost all of the wafer but region B, which is at the edges of the wafer is of higher thickness. The reason of this is that due to surface tension the liquid film is thicker at the edges which gives rise to thicker oxide.

(*b*) *Evaluation*

The deposited oxide is evaluated by infrared spectroscopy, *p*-etch and refractive index measurement. Some meachanical properties are also evaluated.

Infrared spectroscopy.—The half widths and position of bands near 1090 $cm.^{-1}$ and 805 $cm.^{-1}$ in the infrared spectra of SiO_2 is greatly influenced by the bonding character, stoichiometry, density and porosity of the films. All infrared spectra is taken on double beam Carl Zeis instrument. In all cases, a bare silicon wafer of the same thickness is placed in the reference beam to eliminate lattice absorption of silicon.

Figure 2 shows the spectra of as-deposited film. The main bands are 450 cm^{-1}, 805 cm^{-1} and 1070 cm^{-1}. The weak band at 935 cm^{-1} is attributed to silanol group. The film is subjected to densification at 800° C for 15 min in steam and purified dry nitrogen atmosphere. The spectra are shown in Fig. 3. The Si–O stretching band shifts to higher frequency and the half-widths are reduced. By comparing the figures in Table I we conclude that steam densification is more efficient. Also the band at 935 cm^{-1} is removed. To test the moisture stability, the film after densification, is boiled in water for one hour but there is no significant water pick-up which could be detected by infrared spectroscopy.

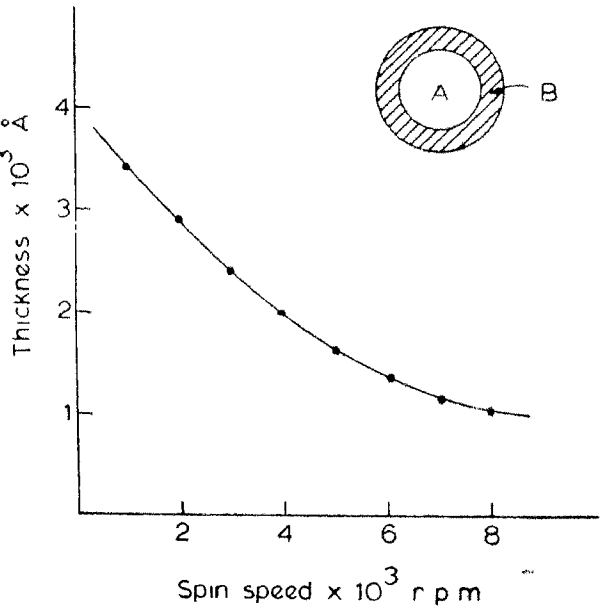

FIG. 1. Oxide thickness *vs.* speed of the spinner. Inset shows two regions of oxide layer for speeds <3,000 rpm.

P-etch technique.—A very commonly used etchant is P-etch [5] in which the etch rate is highly dependent upon density, bondstrain and porosity and the etch rate is a good indication of the film quality.

The P-etch rate of as deposited film is very high but can be reduced drastically by the heat treatments. The various values are given in Table II from which we conclude the steam densification is the best.

Thickness, Refractive index and density.—The as deposited film is porous and can be densified by heat treatments as described earlier. After the densification there is a marked change in thickness, refractive index and density. The various values are shown in Table III.

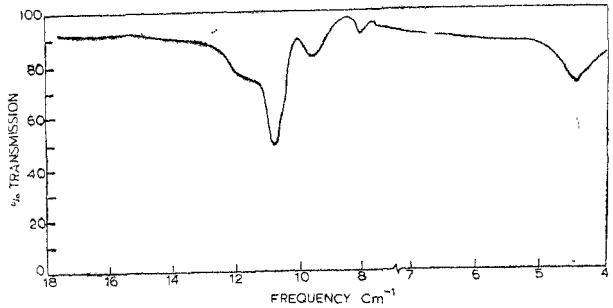

FIG. 2. The I.R. spectra of as-deposited film. The bands are at lower frequency and band widths are more.

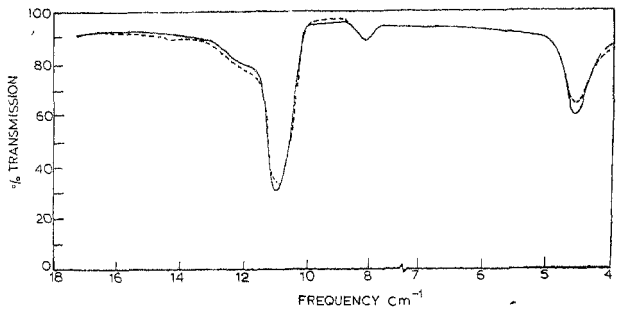

FIG. 3. The I.R. spectra after densification; continuous line ———, densification in steam for 15 min at 800° C. dotted line ..... densification in dry N_2 for 15 min at 800° C. The Si–O stretching has shifted to higher frequency and band widths are less.

Mechanical property.—The oxide film was found to have good mechanical properties. Sharply defined scratch marks can be made without the formation of any crack. Indentation tests were also carried out on the oxide film. A sharp diamond point (136° apex angle, square based pyramid) was pressed against the film and successively weights are added and the point was viewed through a microscope. The weight for which the film develops

TABLE I

Deposition and densification treatment	Band position cm^{-1}	Half-width cm^{-1}
As-deposited film ..	1070	90
Densified in dry N_2 for 15 min. at 800° C ..	1080	86·5
Densified in steam for 15 min. at 800° C ..	1090	83·4

TABLE II

Deposition and densification treatment	Etch rate Å/sec
As-deposited ..	Very high
Densified at 350° C in air for 15 min. ..	15
Densified at 800° C in dry N_2 for 15 min. ..	3
Densified at 800° C in steam for 15 min. ..	2·5

TABLE III

Densification treatment for 15 min.	Thickness Å	refractive index	Density g/c.c.
As-deposited ..	1049	1·430	2·01
In air at 350° C	920	1·432	2·05
Dry N_2 at 800° C	875	1·451	2·12
Steam at 800° C	975	1·459	2·2

fracture gives a quantitative measure of mechanical strength. For as—deposited film, the required weight is 120 gms whereas for stem densified film the required weight it is 155 gm. In Fig. 4 a photomicrograph of the fracture is shown.

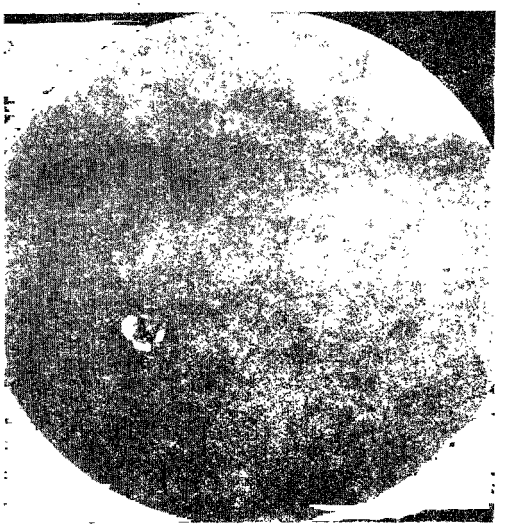

FIG. 4. Photomicrograph of the fracture which shows hair-like lines. Magnification, × 400.

DISCUSSION AND CONCLUSION

A new technique for oxide deposition is described in this paper. The most attractive aspect of this process is that the film is deposited at temperatures as low as room temperature. The apparatus required for depositing a uniform layer is also simple.

The properties of the film are evaluated by the combination of different techniques, *e.g.*, infrared spectroscopy, P-etch rate, refractive index, etc. From the infra-red spectrum of the as-deposited film Fig. 2 it is concluded that the film consists only of SiO_2 because the absorption peaks due to other oxides of silicon (*e.g.*, SiO and Si_2O_2) are absent. By comparing the

infrared spectra of as-deposited film and heat annealed films Fig. 3 it is observed that after heat treatments the absorption peaks are shifted to higher frequencies and bandwidths are reduced. The reason behind this is that the extent of polymerization in the oxide film is increasing and more covalent bonds are produced [6]. The fact that the density of annealed films are higher also supports that higher degree of polymerization is obtained in heat treated films.

From P-etch rate, refractive index and density data it is concluded that the as-deposited film is porous. Porosity of deposited films is a common characteristics and the lower the temerature of deposition, the greater is the porosity. The etch rate is high because the points for chemical attack is more. This porous nature of the film can be removed by densification treatments described earlier and the etching properrty is improved. In some photolithographic processes, sometimes it may however be, desirable to have a layer with high-etch rate [7].

Steam densification is found to be more efficient than other processes. In this process a thin layer of thermal oxide (≈ 100 Å) is produced. But this thin layer cannot account for all the improvements as it can be seen that there is a very little differences between the properties of purified dry nitrogen densified and steam densified films.

Mechanical properties are helpful in evaluating the adhesion of the film to the substrate. It is found that after heat treatment the adhesions is very strong so that when scratches are made there is no peel off along the scratch edges.

ACKNOWLEDGEMENT

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Calendar of events: Conferences/Symposia at the Indian Institute of Science Campus

Sl. No.	Name of the School	Period	Sponsoring Department of the Institute
1.	50th Symposium of Biochemical Society	9–10 January 1976	Biochemistry
2.	QIP—"Design and Performance Estimation of Heat Exchangers"	1–14 February 1976	Mechanical Engineering
3.	"Design and Technology of Digital Equipment"	9–21 February 1976	Electrical Communicatic Engineering
4.	"Dynamics and Control of Industrial Organisers"	12–25 February 1976	Chemical Engineering
5.	QIP—"Public Water Supply Systems"	16–29 February 1976	Chemical Engineering
6.	QIP—"Dynamics of Engineering Systems"	1–15 March 1976	School of Automation and Mechanical Engineering
7.	QIP—"Limit State Design of Concrete Structures"	8–20 March 1976	Chemical Engineering
8.	"Applications of Computers for Load Despatch"	17–23 March 1976	School of Automatio and Aeronautical Engineering
9.	"An Intensive Course on Active and Digital Filters"	19 April to 2 May 1976	Metallurgy
10.	"Recent Developments in Physical Metallurgy—Techniques"	6–12 May 1976	Metallurgy
11.	QIP—"Insulation Problems in High Voltage Engineering"	9–23 May 1976	High Voltage Engineering
12.	"Particle Size Analysis and Separation"	14–29 May 1976	Metallurgy
13.	"Refresher Course Short Term Institute"	14 June to 13 July 1976	Microbiology apd Cel Biology Laborator
14.	"Advanced Institute on Reaction Mechanisms All India, University and College Teachers"	16 June to 13 July 1976	Organic Chemistry
15.	"Advanced Summer Institute in Theoretical Plasma Physics"	June–July 1976	Physics

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