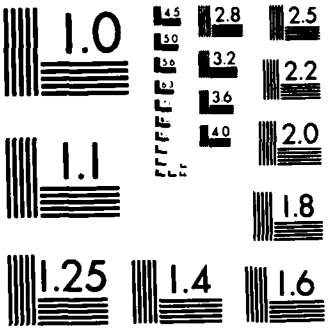
AD-A171 796 SILICON OXIDATION AND SIO2 INTERFACE OF THIN OXIDES(U) 1/1
NORTH CAROLINA UNIV AT CHAPEL HILL DEPT OF CHEMISTRY
N M RAVINDRA ET AL. 29 JUL 86 TR-9 N00014-86-K-0305
UNCLASSIFIED F/G 20/12 NL



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Contract No. N00014-86-K-0305

TECHNICAL REPORT NO. 9

Silicon Oxidation & SiO_2 Interface of Thin Oxides

by

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in

The Journal of Materials Research (accepted for publication)

A171 796

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION: Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S): Technical Report #9

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION: UNC Chemistry Dept.

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION: Office of Naval Research (Code 413)

6c. ADDRESS (City, State and ZIP Code)
11-3 Venable Hall 045A
Chapel Hill, NC 27514

7b. ADDRESS (City, State and ZIP Code)
Chemistry Program
800 N. Quincy Street
Arlington, Virginia 22217

8a. NAME OF FUNDING/SPONSORING ORGANIZATION: Office of Naval Research

8b. OFFICE SYMBOL (If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: Contract #N00014-86-K-0305

8c. ADDRESS (City, State and ZIP Code)
Chemistry Program
800 N. Quincy, Arlington, VA 22217

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.

11. TITLE (Include Security Classification) SILICON OXIDATION & SiO$_2$ INTERFACE OF THIN OXIDES

12. PERSONAL AUTHOR(S): NM Ravindra, J. Narayan, Dariush Fathy, JK Srivastava and Eugene A. Irene

13a. TYPE OF REPORT: Interim Technical

13b. TIME COVERED FROM ________ TO ________

14. DATE OF REPORT (Yr., Mo., Day): 7/29/86

15. PAGE COUNT: 16

16. SUPPLEMENTARY NOTATION: Prepared for publication in The Journal of Materials Research

17. COSATI CODES

FIELD	GROUP	SUB. GR.

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☒ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION: Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL: Dr. David Nelson

22b. TELEPHONE NUMBER (Include Area Code): (202) 696-4410

22c. OFFICE SYMBOL

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PA

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ABSTRACT - High Resolution Transmission Electron Microscopy (HRTEM) and ellipsometry techniques have been employed to measure thicknesses of silicon oxide, grown at 800°C in dry oxygen, in the thickness range of 2 to 20 nm. While the oxide growth data measured from TEM obey a linear behavior, those obtained from ellipsometry are seen to follow a linear-parabolic law. The interface structure as function of the increasing oxide thickness was studied using HRTEM. At these oxidation temperatures, we do not see the earlier reported systematic dependence of roughness at the interface on the oxide thickness for oxides grown at 900°C. Attempts aimed at correlating the high resolution transmission electron micrographs with some physical parameters like the refractive index and the dielectric breakdown lead us to considerations of the importance of the effect of protrusions of silicon atoms of 1nm size into SiO_2 layers on the interface properties. These findings lead us to explain some key features concerning the refractive index, density and dielectric strength of thin SiO_2.

I. INTRODUCTION

Thin gate oxide (SiO_2) in the thickness range of 10 to 20 nm is needed for submicron devices. The formation of reliable and stable thin gate oxides requires detailed understanding of the kinetics in the thin oxide regime and the interface structure as it is known to control defects and dielectric breakdown in oxides. While most of the earlier thickness measurements relied on ellipsometry, in recent years, Transmission Electron Microscopy (TEM) is being widely used to measure thicknesses of thin oxides[1]. Unlike ellipsometry which warrants a knowledge of the correct refractive index of the material under consideration, TEM imposes no such condition.

Inspite of the tremendous efforts being invested today in understanding the Si - SiO_2 interface, some very elementary questions as to the role of the interface in determining the microstructural and electrical properties like breakdown strength of thin SiO_2 and their internal correlations remain unanswered. Even the refractive index of the Si/SiO_2 interface has been debated and remains a disputed issue. In the following study, we attempt to answer some of these questions. We have studied evolution of the (a) oxide growth and (b) Si/SiO_2 interface using High Resolution Transmission Electron Microscopy (HRTEM). The present studies have been carried out on dry oxides grown thermally at 800°C. No attempt has been made here to deliberately incorporate roughness like growing the oxide in a chlorine ambient[2,3]. The formation of protrusions of the silicon atoms into SiO_2 has been studied as a function of increasing oxidation times/ oxide thicknesses. The role of these protrusions in determining the electrical and optical quality of the Si-SiO_2 interface has been qualitatively evaluated.

II. EXPERIMENTAL PROCEDURE

Single crystal silicon wafers (p-type Czochralski) of <100> orientation and 2 ohm.cm resistivity were used for growing the oxides. The cleaning procedure consisted of the conventional RCA technique followed by a HF dip and a thorough rinsing with DI water. Oxides were thermally grown at 800°C for time durations of 1 to 300 minutes. Ultra high purity oxygen ($H_2O < 0.5$ ppm) was used in the oxidation process.

Oxide thickness measurements were made employing carefully aligned Gaertner manual and automatic ellipsometers. The agreement in the thicknesses obtained from both the ellipsometers were within 0.5nm. Ion-beam thinning procedure was used to prepare cross sections for HRTEM studies. High resolution phase contrast images of the interface were taken at Scherzer optimum defocus value of 65nm and <110> orientation using a JEOL(200CX) TEM at 200 KV with a 0.26nm point to point resolution.

III. RESULTS & DISCUSSION

We present a summary of the oxide thickness measurements in Table 1. As can be seen in the table, the oxide thicknesses obtained by ellipsometry are within 1nm of those measured from TEM. The results of these measurements are plotted in Fig.1. Two very thin and two very thick samples (A through D) were chosen for HRTEM studies. In Fig.1, it is seen that the oxide growth data obtained from ellipsometry is non-linear with time. However, the growth data obtained from TEM is fairly linear. Many empirical and semi-empirical relationships have been proposed to model oxide growth in the thin oxide growth regime. These include varieties of linear, parabolic, exponential forms and their combinations[4]. Using conventional fitting procedures, we find that a linear-parabolic equation of the form,

$$t = A_0 + A_1 d + A_2 d^2 \quad \text{(i)}$$

represents the best fit to the ellipsometry data. In the above equation, t is the time and d is the oxide thickness, A_0, A_1 and A_2 are the fitting parameters. The detailed evaluation of the relevant fitting parameters and their interpretation is beyond the scope of the present work. Similar measurements of the oxide thickness in the thin oxide regime has been recently reported by Carim and Sinclair[1]. It is interesting to note that our results of the growth rate behavior obtained from TEM and ellipsometry are similar to those reported earlier[1] despite the major differences in the method of growth of the oxide in the two cases. In the present study, the oxides have been grown at 800°C in dry O_2 while they[1] grew the oxides at 900°C in an ambient of 10% dry O_2 in Ar.

There are many methods of determining the oxide thickness. These include ellipsometry, transmission electron microscopy, Auger spectrsocopy and capacitance-voltage measurements. Generally, thicknesses evaluated from the Auger spectra are about 1nm less[5] than those evaluated from ellipsometry. A large part of this discrepancy has been attributed to the existence of an interface layer containing mostly SiO[6]. Due to the presence of this silicon-rich oxide[7], oxide thickness evaluated from TEM is expected to be ~0.5nm higher than that evaluated from ellipsometry. After all, phase contrast electron microscopy is not able to differentiate between these two amorphous media. In principle, ellipsometry is a very well-accepted technique for thickness and refractive index measurements of thin transparent films. However, when the thickness of the film is less than ~100nm, refractive index measurements become difficult and unreliable. A proper alignment of the involved optics in the ellipsometer along with the relevant and appropriate optical constants of the film and the substrate is expected to improve the reliability of the measurements of thicknesses of thin films. Electrical measurements like high frequency capacitance - voltage could be employed to evaluate the oxide thickness. But, the sources of error are essentially due to (a) uncertainty in the measurement of the diameter of the real MOS device, (b) corrections in the dielectric constant due to the silicon rich oxide and (c) possible series resistance effects.

As can be seen in Fig.1, we do not see a consistent increase in the thickness evaluated from TEM over the respective value determined from ellipsometry for the same sample. On the other hand, the ellipsometry data of Carim and Sinclair[1] yields thicknesses consistently higher than those measured from TEM (see inset, Fig.1). Further, there are significant differences between their TEM and ellipsometry data.

The image of the Si/SiO_2 including the interface of sample C shown in Fig.2 indicates that the oxide thickness is quite uniform. Such images have been employed to determine the oxide thickness. At least, for these dry oxides grown at 800°C, we do not observe significant non-uniformities in the oxide thickness. Further, from the results of the HRTEM of the Si/SiO_2 interface of samples A, B, C and D in Fig.3 & 4, it is clear that the sample D has the roughest of the interfaces. Carim and Sinclair[1] report that, for SiO_2 grown at 900°C, the interface roughness attains a maximum value of 1.4nm at an oxide thickness of ~4nm and decreases with increase in oxide thickness. The choice of our samples A, B, C & D was essentially aimed at investigating this interesting dependence of roughness at the interface on oxide thickness. The oxide thickness increased monotonically from A to D. As is seen in Figs. 3 & 4, at least to a first approximation, we do not see any correlation between roughness at the interface and the oxide thickness in our measurements for oxides grown at 800°C. In fact, the thickest oxide seems to have the roughest interface with protrusions of silicon atoms of the order of ~1nm. Of all the samples considered in these figures, sample C appears to have the smoothest of the interfaces. Our recent studies of Si/SiO_2 interfaces show roughnesses of a similar magnitude even for the oxides grown at 1000°C[8]. Protrusions of silicon atoms of the order of ~1nm are observed in Fig. 4 for sample D.

Although, in general, oxides are characterized as good quality oxides depending on their (1) defect density and (2) breakdown strength, no clear correlation between these two properties and roughness at the interface has been established. As a first implication, roughness at the interface results in (a) increasing the effective area of the interface which will reduce the mobility of charge carriers in MOS based devices, (b) a local field enhancement across the oxide which should help in the oxide breakdown processes at lower voltage. However, such protrusions or hillocks can act as electron emitters thus reducing the positive charge centers near the interface. Thus, roughness of the order of magnitude of 1nm at the Si/SiO_2 interface in 20nm thick oxide is not expected to affect the performance characteristics of MOS based devices very much. Of course, to a first approximation, mobility of charge carriers is expected to decrease slightly in such devices. Although the starting wafer is believed to have a tremendous influence on the quality of the oxide grown on it[9], the interface roughness is expected to depend upon the interfacial stress.

STRESS - REFRACTIVE INDEX CONSIDERATIONS

Mechanisms involved in the evolution of the interface roughness with increasing oxide thickness have already been explained earlier[1]. Essentially, stress relaxation, strain distribution and diffusion limited processes (in thick oxides) are expected to play decisive roles in determining the roughness at the interface. At 800°C, the stress relaxation time is known to be about 5100 hrs[10] while at oxidation temperatures of 900°C, it has been evaluated to be 21 hrs[10]. These large relaxation times reported in the literature for oxides grown respectively at 800 and 900°C make it difficult to explain the above observed differences in the behavior of interface roughness versus oxide thickness as function of oxide growth temperatures. After all, in both these cases, stress is expected to be accumulated at the interface. For higher processing temperatures (950-975°C), once the viscous flow sets in, stress is relieved during oxidation. The intrinsic stress, which is the difference of the total film stress and the thermal expansion stress, should help in explaining the dependence of the roughness at the interface on oxide thickness. At present, enough theoretical or experimental evidences are not available to suplement the above observations with stress versus thickness data as function of oxide growth temperatures. Stress measurements for oxides with thicknesses $<$ 100nm are quite cumbersome with present day experimental methods.

Generally, it is accepted that a thinner oxide is under a higher stress distribution (defined as, stress/thickness) than a thicker oxide. This is expected to bring the molecules of SiO_2 closer to each other in a thin oxide, resulting in a higher packing density (i.e., the number of molecules/volume). This should result in increased densities. A lower stress in an oxide grown at a higher temperature is expected to decrease the packing density and hence increase its transparency to optical photons. Thus, the refractive index should decrease with increase in temperature of oxide growth. These conclusions are in complete accord with the experimental observations of Taft[11], and Irene and co-workers[10,12]. Evidently, because of higher stress distributions, thin oxides are expected to have densities higher than thick oxides. Presuming that intrinsic dielectric breakdown involves breaking the molecules, we are inclined to believe that dielectric breakdown in SiO_2 is very much dependent on the structure of SiO_2. A low breakdown strength of SiO_2 is indicative of its higher disorder. These qualitative arguments help in understanding the experimental fact that, generally, thin oxides have a higher breakdown strength than thick oxides[13].

All the above qualitative conclusions, concerning the dependence of the refractive index and density on temperature of oxide growth, are in accord with our experimental findings. Using ellipsometry, we have deduced the refractive indices of ~100nm thick oxides grown at different temperatures[14]. Utilizing the following Lorentz-Lorenz relation, we evaluate the density of SiO_2 as function of temperature;

$$((n^2 - 1)/(n^2 + 2))(M/\rho) = (4\pi/3)N\alpha \quad \text{(ii)}$$

(in e.s.u) where, n is the refractive index, M is the molecular weight, ρ is the density, N is the Avogadro number and α, the total polarizability of the molecule. Since, in the optical range, the dielectric constant arises essentially from the electronic polarizability α_e, $\alpha = \alpha_e$ in relation (ii). Thus, density follows as,

$$\rho = (3M/4\pi N\alpha_e)((n^2 - 1)/(n^2 + 2)) \qquad \text{(iii)}$$

It may be noted here that the extrapolation of the application of the Lorentz-Lorenz relation to amorphous materials has been reported earlier[15]. Utilizing the known values of α_e available in the literature and assuming it to be constant, values of the density have been estimated. In Fig.5, n is plotted versus ρ for SiO_2 grown on Si, as function of temperature of growth. As can be seen in the figure, with increase in temperature of oxide growth, the refractive index decreases and so does the density. This result is in accord with that of

Taft[11] who reports a similar decrease in n with increase in temperature of growth of SiO_2. Our estimates of the density are comparable with the values cited in the literature (see, for example, Sze[16], $\rho = 2.2$ gms/cc). In these calculations, the extinction coefficient of SiO_2 has been neglected, since the absorption in SiO_2 is small at measured wavelengths of n (632.8 nm).

IV. SUMMARY

Thicknesses of SiO_2, grown thermally on Si at 800°C for time durations of 1 to 300 minutes in dry O_2, have been measured using the techniques of High Resolution Transmission Electron Microscopy (HRTEM) and ellipsometry. While the oxide thickness versus time data obtained by ellipsometry is seen to obey the linear-parabolic law, those measured from TEM follow an almost linear behavior. The two sets of thickness data have been seen to be within 1nm of each other. The Si/SiO_2 interface roughness has been studied using HRTEM. Comparisons have also been made with the available literature on the oxide growth and the evolution of the interface roughness with oxide thickness. At least for these dry oxides grown at 800°C, no systematic dependence of the interface roughness on the oxide thickness is noted. Interpretations for these results have been sought from stress considerations. The dependence of the refractive index, density and dielectric strength of SiO_2 on its thickness and growth temperatures has also been discussed.

ACKNOWLEDGEMENTS

We thank Dr. Carl Osburn for fruitful discussions. We are grateful to the Microelectronics Center of North Carolina for permitting us to use the facilities. Two of the authors (JKS & EI) acknowledge with thanks the financial support of the Office of Naval Research.

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TABLE I - Summary of the oxide thickness measurements. All thicknesses represent average values.

Sample	Oxidation Time (minutes) at 800^{0}C	Oxide Thickness (nm) Ellipsometry	TEM
A	1	2.0	3.0
	5	3.1	
B	10	3.7	3.5
	20	5.2	
	40	6.7	
C	100	10.8	9.5
	200	16.6	
D	300	21.3	22.0

FIGURE CAPTIONS

Figure 1 - Oxide growth data. Some of the thicknesses are compared with those evaluated from TEM. Figure inset ; Oxide growth data of Carim and Sinclair[1].

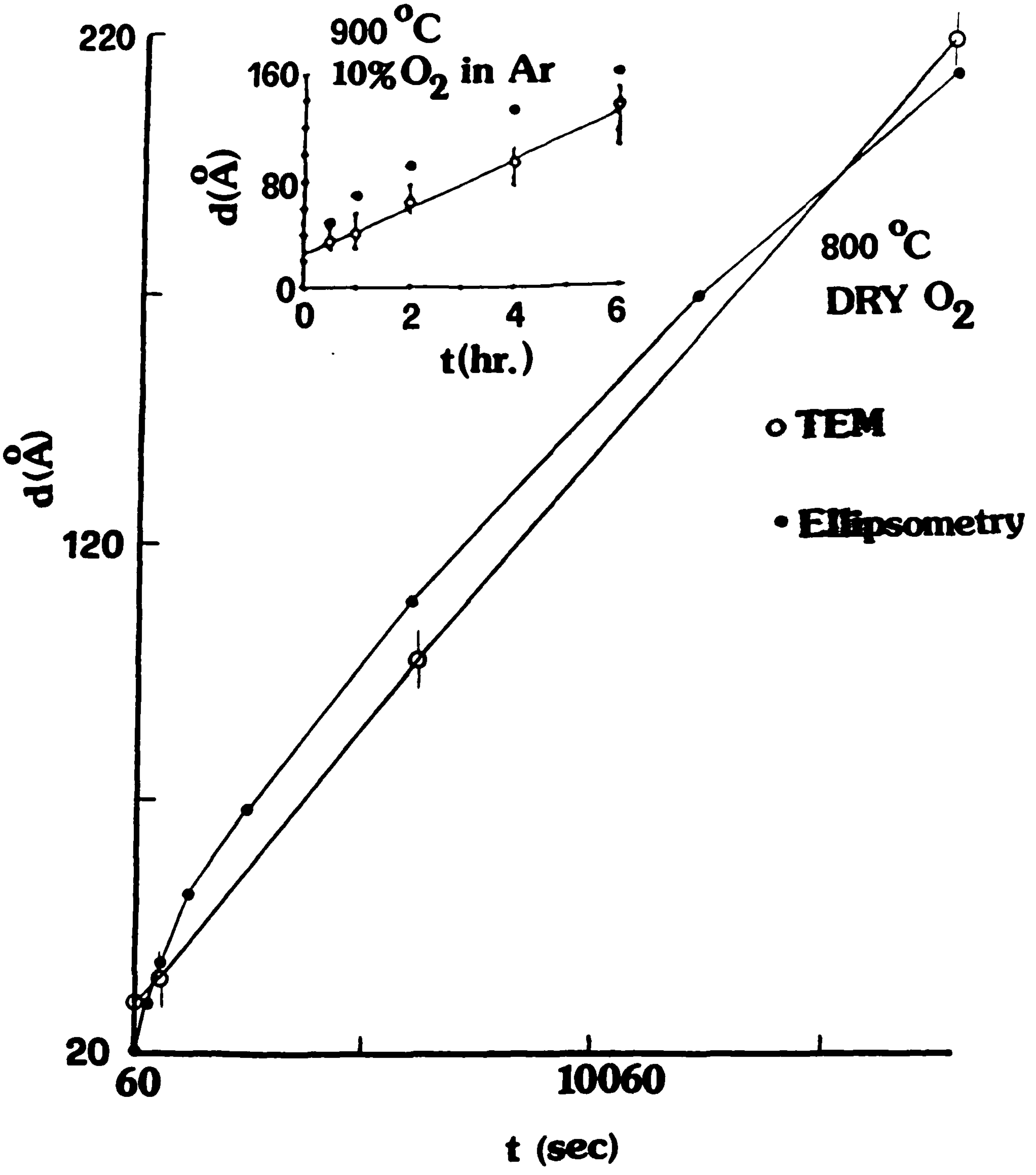
Figure 2 - Low magnification image of the Si/SiO_2 interface of sample C.

Figure 3 - High Resolution Transmission Electron Micrographs of the Si/SiO_2 interface for samples of different thicknesses. The circled areas have been further magnified in the next figure.

Thicknesses are; A - 3.0nm, B - 3.5nm, C - 9.5nm, D - 22.0nm

Figure 4 - High Resolution Transmission Electron Micrographs of the circled areas of Fig. 3.

Figure 5 - Refractive index n versus density ρ as function of temperature of oxide growth for ~100nm thick SiO_2.



220
120
20
d(Å)
60
10060
t (sec)
900 °C
10% O_2 in Ar
160
80
0
d(Å)
0
2
4
6
t(hr.)
800 °C
DRY O_2
○ TEM
● Ellipsometry

FIG. 1

FIG.2

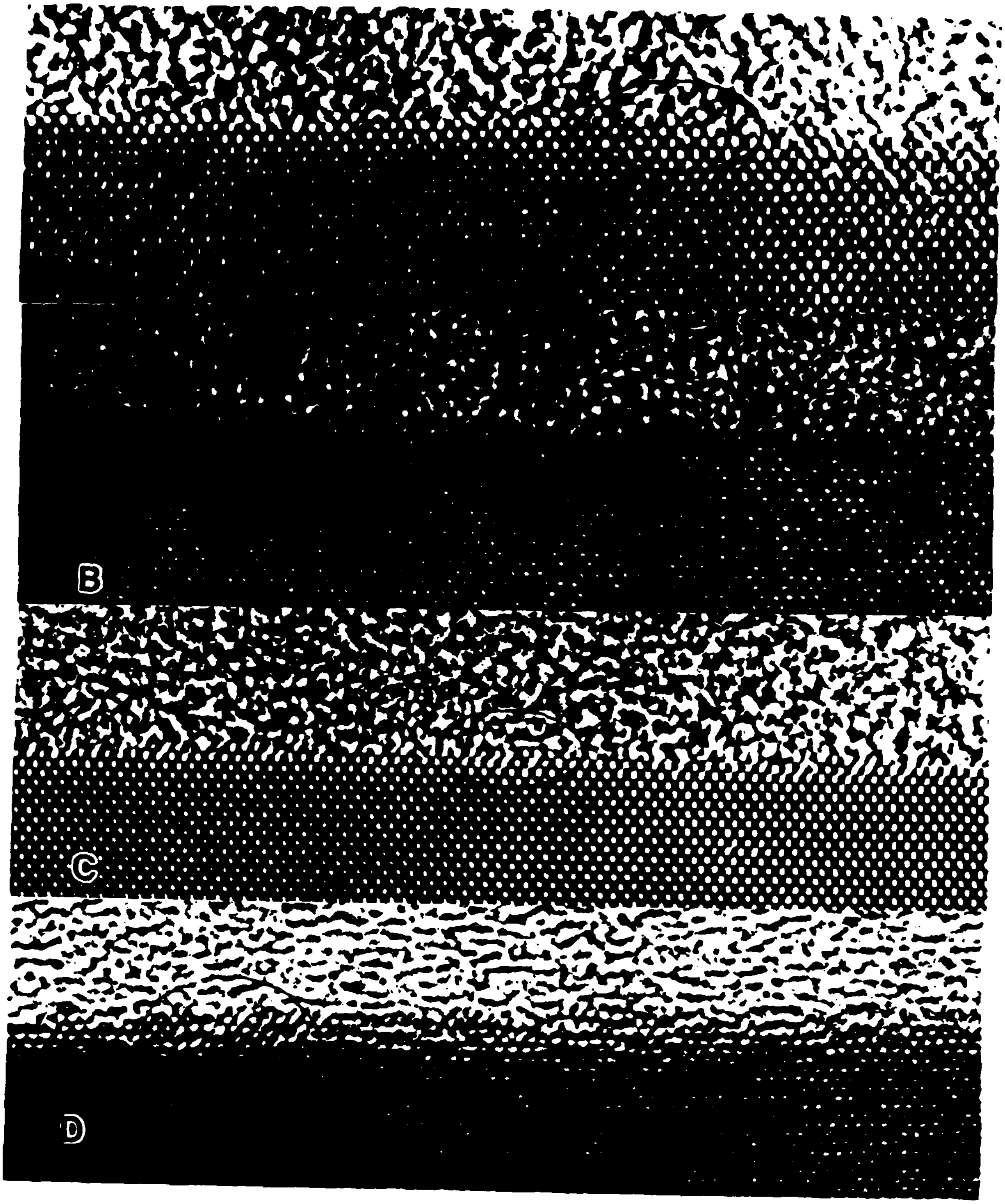
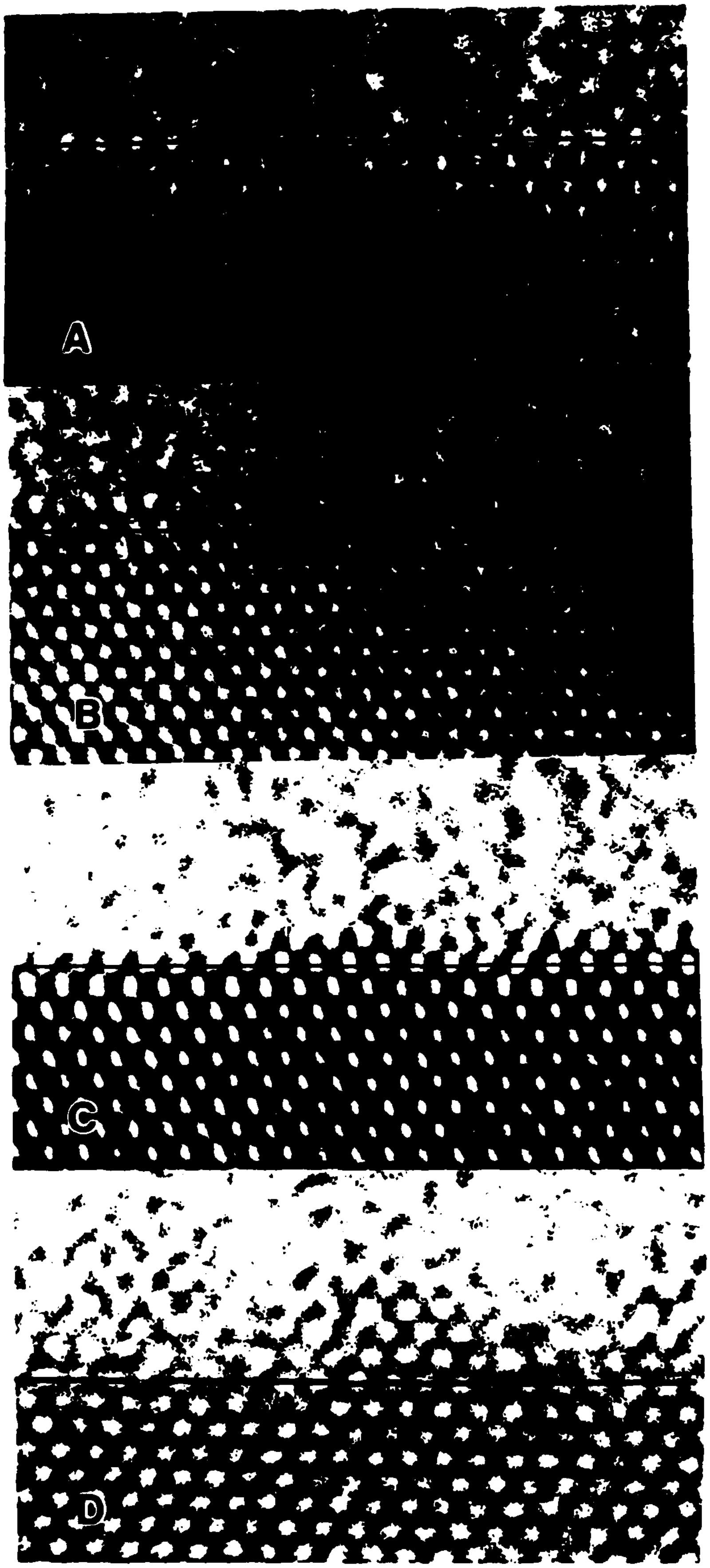


FIG.3


A
B
C
D

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