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GRANT N00014-89-J-1178

R&T Code 413q001-01

TECHNICAL REPORT NO. 30



Refractive Index Profiles of Thermally Grown and  
Chemically Vapor Deposited Films on Silicon

by

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Submitted to the  
Journal of Electrochemical Society

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## REPORT DOCUMENTATION PAGE

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|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------|------------------------------------------------------------------------------------------------------------------|----------------------|----------|
| 1a. REPORT SECURITY CLASSIFICATION<br>Unclassified                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                          | 1b. RESTRICTIVE MARKINGS                                                                                         |                      |          |
| 2a. SECURITY CLASSIFICATION AUTHORITY                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                          | 3. DISTRIBUTION/AVAILABILITY OF REPORT<br>Approved for public release; distribution unlimited.                   |                      |          |
| 2b. DECLASSIFICATION/DOWNGRADING SCHEDULE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                          |                                                                                                                  |                      |          |
| 4. PERFORMING ORGANIZATION REPORT NUMBER(S)<br>Technical Report #30                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                          | 5. MONITORING ORGANIZATION REPORT NUMBER(S)                                                                      |                      |          |
| 6a. NAME OF PERFORMING ORGANIZATION<br>UNC Chemistry Dept.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | 6b. OFFICE SYMBOL<br>(If applicable)     | 7a. NAME OF MONITORING ORGANIZATION<br>Office of Naval Research (Code 413)                                       |                      |          |
| 6c. ADDRESS (City, State and ZIP Code)<br>CB# 3290, Venable Hall<br>University of North Carolina<br>Chapel Hill, NC 27599-3290                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                          | 7b. ADDRESS (City, State and ZIP Code)<br>Chemistry Program<br>800 N. Quincy Street<br>Arlington, Virginia 22217 |                      |          |
| 8a. NAME OF FUNDING/SPONSORING ORGANIZATION<br>Office of Naval Research                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 8b. OFFICE SYMBOL<br>(If applicable)     | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER<br>Grant #N00014-89-J-1178                                       |                      |          |
| 8c. ADDRESS (City, State and ZIP Code)<br>Chemistry Program<br>800 N. Quincy Street, Arlington, VA 22217                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                          | 10. SOURCE OF FUNDING NOS.                                                                                       |                      |          |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                          | PROGRAM ELEMENT NO.                                                                                              | PROJECT NO.          | TASK NO. |
| 11. TITLE (Include Security Classification) REFRACTIVE INDEX PROFILES OF THERMALLY GROWN AND CHEMICALLY VAPOR DEPOSITED FILMS ON SILICON                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                          |                                                                                                                  |                      |          |
| 12. PERSONAL AUTHOR(S)<br>S. Chongsawangvirod and E.A. Irene                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                          |                                                                                                                  |                      |          |
| 13a. TYPE OF REPORT<br>Interim Technical                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | 13b. TIME COVERED<br>FROM _____ TO _____ | 14. DATE OF REPORT (Yr., Mo., Day)<br>January 18, 1990                                                           | 15. PAGE COUNT<br>27 |          |
| 16. SUPPLEMENTARY NOTATION<br>REFRACTIVE INDEX PROFILES OF THERMALLY GOWN & CHEMICALLY VAPOR DEPOSITED FILMS ON SILICON                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                          |                                                                                                                  |                      |          |
| 17. COSATI CODES                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                          | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)                                |                      |          |
| FIELD                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | GROUP                                    |                                                                                                                  |                      | SUB. GR. |
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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                          |                                                                                                                  |                      |          |
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| 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT<br>UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS <input type="checkbox"/>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                          | 21. ABSTRACT SECURITY CLASSIFICATION<br>Unclassified                                                             |                      |          |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL<br>Dr. David L. Nelson                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                          | 22b. TELEPHONE NUMBER<br>(Include Area Code)<br>(202) 696-4410                                                   | 22c. OFFICE SYMBOL   |          |

## REFRACTIVE INDEX PROFILES OF THERMALLY GROWN AND CHEMICALLY VAPOR DEPOSITED FILMS ON SILICON

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### Abstract

Ellipsometry, although used extensively in the microelectronics field for the measurement of film thicknesses and refractive indices, does not usually yield reliable refractive indices for dielectric films less than 50 nm thick due to instrumental errors and software limitations. Addressing this issue, we report ellipsometric procedures that enable a reliable assessment of refractive index profiles for a variety of thermally grown and chemically vapor deposited, CVD, dielectric films on Si substrates down to about 10 nm thickness and we compare the results in terms of the current understanding about the film-substrate interface. In all cases studied we find that the interfacial region is optically different than the thick film, and that the precise film processing substantively alters the nature of the interface region.

### Introduction

Previous ellipsometric measurements (1,2) have shown that thermally grown  $\text{SiO}_2$

films on Si are optically different near the interface yielding higher refractive indices,  $N_f$ , than for  $\text{SiO}_2$  further away from the interface. Our recent work (3) confirmed these results (1,2) by using a comparison of ellipsometric measurements and transmission electron microscopy, TEM. We established a novel ellipsometry approach in which both the instrumental and the data reduction errors are compared with the ellipsometric measurements on thin oxide films that were less than 100 nm thick. This new technique enabled the refractive index profile for  $\text{SiO}_2$  films down to about 10 nm to be distinguished from the usual error associated with ellipsometric measurement. The higher refractive indices measured for the very thin oxide films were successfully explained (3) with the use of a previously proposed (1,2) continuously graded interlayer model. The  $\text{SiO}_2$  refractive index profile from the interface to the bulk was found to be oxidation temperature dependent (3), and in essential agreement with X-Ray photoelectron spectroscopy, XPS, (4) and film stress studies (5) which indicate a gradual change from the interface to bulk structure.

The present study utilizes the novel ellipsometric technique to examine the refractive index profiles of thermally grown and chemical vapor deposited, CVD, films on single crystal silicon substrates under various experimental conditions and down to film thickness of 10 nm. We report that both thermal and CVD  $\text{SiO}_2$  films on Si yield larger refractive indices near the Si- $\text{SiO}_2$  interface in agreement with our earlier report (3). CVD  $\text{Si}_3\text{N}_4$  has been found to yield lower refractive indices near the Si-nitride film interface indicating the presence of an oxide film existing before or during deposition. Results from refractive

index profiles of  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  films are determined by two independent experiments. In one experiment, films are grown to various thicknesses, while the other uses films that are chemically thinned. Results from these two experiments are compared and suggest complex behavior due to the influence of  $\text{H}_2\text{O}$  and chemical etchant on the films. A comparison of wet and dry thermally grown  $\text{SiO}_2$  film reveals different index profiles and this is modeled in the context of other studies.

### Experimental Procedures

The films used in this study were prepared by thermal oxidation and CVD onto commercially available single crystal (100) Si wafers lightly n and p doped. No systematic differences due to dopant type or amount were seen or expected. The thermal oxidations were performed at 1 atm at temperature ranging from  $800^\circ$  -  $1000^\circ\text{C}$  in a conventional double walled fused silica oxidation furnace. In the case of dry oxidation, the water content of the  $\text{O}_2$  gas was measured at the furnace exit, and found to be less than 2 ppm when preburner-condenser apparatus was placed before the oxidation furnace (6). For wet oxidations, a fused silica water bubbler was used in place of the preburner-condenser apparatus. The Si wafer cleaning procedure performed immediately before oxidation consisted of a modified RCA clean (7) followed by a 10 second HF dip and thorough deionized, DI, water rinse. Unless otherwise mentioned the data on various film thicknesses were obtained by chemically etching back as grown films of about 100 nm thick using a buffered HF solution ( $50:1/\text{NH}_4\text{F}:\text{HF}$ ) followed by DI water rinse. In order to

verify that the high  $N_f$  observed in the initial thin regime of  $\text{SiO}_2$  is real, a series of oxides from 15-100 nm were thermally grown to the various thicknesses and compared to the chemically thinned oxides. These two kinds of samples will be referred to in the later discussion as "as-grown" and "etch-back" samples. The CVD oxide process consisted of an argon sputter clean at  $150^\circ\text{C}$  followed by electron cyclotron resonance plasma enhanced chemical vapor deposition, ECR PECVD, at a substrate temperature of  $100^\circ\text{C}$ . Silicon nitride films were deposited at various thicknesses using both low pressure chemical vapor deposition, LPCVD and PECVD at  $380^\circ\text{C}$  using research grade purity  $\text{SiH}_4$  and  $\text{NH}_3$  gases. The wafers used in the nitride CVD were pre-cleaned by (10:1/DI:HF) solution. The refractive index and thickness measurements were obtained using a frequently aligned (both angle of incidence by an autocollimation procedure and polarization component offsets) research quality ellipsometer. The ellipsometric measurement was a null two zone measurement using the polarizer, compensator, sample, analyzer, PCSA, configuration with a He-Ne light source at 632.8 nm. Component azimuths and angle of incidence are known to  $0.01^\circ$ . The data reduction algorithms use both a random search routine which leads to non-directional un-biased results, and a minimal error convergence routine where the solution for the refractive index and the thickness is precise to  $10^{-6}$  in the refractive index,  $\Delta$ , and  $\Psi$ . We will refer to this later as an "exact" solution, since any error introduced by this routine is far smaller than the other sources of error. The Si complex index used in this research was  $3.868 - i.024$

## Results and Discussion

As was shown to be important in a previous study (3), we herein report the experimental  $N_f$  values along with the composite error curves. As was discussed in detail (3), the composite error curves contain the random errors that can be determined including truncation errors, optical component errors, and alignment errors. From this representation, one can discern trends in the data that are outside of the uncertainties of the measurement and therefore significant.

### Thermally Grown and CVD Silicon Dioxide Films

Figure 1 shows the measured  $N_f$  values for both thermal and ECR PECVD  $\text{SiO}_2$  films all of which display an increase in refractive index as the Si- $\text{SiO}_2$  interface is approached as the films are chemically thinned toward the interface. The random error envelope considers the errors around the value of 1.465 for the  $\text{SiO}_2$  index which is the value obtained for thick  $\text{SiO}_2$  films grown at  $1000^\circ\text{C}$  in dry  $\text{O}_2$ . For the thermal oxides, we believe that several well known effects contribute to the observed thermal oxide refractive index profiles. First, the  $N_f$  ordering for the thicker  $\text{SiO}_2$  films is explained by considering the viscoelastic relaxation of the bulk oxide which is dependent on oxidation temperature (8). During oxidation, the oxide forms under compression due to the molar volume change and undergoes relaxation at the oxidation temperature which lowers the compressive stress and hence the density and  $N_f$ . This effect is seen in the relative order of  $N_f$  with oxidation temperature for  $\text{SiO}_2$  films thicker than 30 nm and agrees with

previous studies (5,8,9) which show a higher  $N_f$  for lower oxidation temperature. Near the Si-SiO<sub>2</sub> interface, more complicated behavior is observed. Previously, this interface has been represented by using a temperature dependent continuously graded index interlayer optical model (3). This model is in accord with stress measurements (10) which show a compressively stressed higher density oxide near the Si-SiO<sub>2</sub> interface. However, for films thinner than 30 nm there is no apparent order with oxidation temperature as was seen for the thicker films. The error curves show that the random errors have a greater effect on the refractive index calculation for the thin films. Hence, the larger error associated with the thin film measurement is the likely reason for the randomization of the order, but we will show later in this paper that chemical etching may also contribute to the lack of a trend for thin films.

Also seen in Fig. 1, the PECVD SiO<sub>2</sub> films deposited at a substrate temperature of about 100°C show consistently lower  $N_f$  values than the thermally grown films. The fact that a higher index is observed at smaller film thickness for PECVD films suggests that there is some degree of interaction between surface Si atoms and the deposited oxide during deposition. Because of the lower deposition temperatures it seems reasonable that the PECVD process should yield a thinner transition region as compared to the higher temperature grown thermal oxides. However, there exists recent evidence for an oxidation reaction occurring at the Si-SiO<sub>2</sub> interface during PECVD deposition of SiO<sub>2</sub> thin films on Si both by Auger electron spectroscopy, AES (11) and infrared absorption spectroscopy, IR (12). Medium energy Rutherford back scattering ion beam channeling measurements

(13) showed no measurable difference in interface sharpness and elemental structures for PECVD and thermal oxides. Thus, the slightly lower  $N_f$  values observed for the PECVD films compared to the thermal oxides may only be partly due to the reduced intermixing at the interface. For a purely CVD film, only a thermal stress component is operative, since no volume change occurs due to the interface reaction as for thermal oxidation. In fact the value of compressive stress in the vicinity of the Si-SiO<sub>2</sub> interface for the deposited oxide films is found to be lower than for the thermal oxides (12) because the extent of the reaction at the interface is likely less than for the oxidation situation. Thus smaller but not zero stress would result for the PECVD films near the interface, hence the smaller increase in  $N_f$  is to be expected.

### CVD Silicon Nitride Films

The refractive index versus thickness profiles for both LPCVD and PECVD Si<sub>3</sub>N<sub>4</sub> as-grown films display a decrease in  $N_f$  as film thickness decreases as shown in Fig. 2. The decreasing  $N_f$  trend near the interface could be explained by modelling an additional lower index layer on top and/or beneath the nitride film. The inner low index film could be explained by the existence of an oxygen enriched layer or a native oxide (of lower index) under the silicon nitride film (14), or by the microscopic surface roughness which could increase the probability of void formation (15). This void model considers that during the film deposition upon a rough surface, shadowed regions are left uncovered by the incoming atoms, therefore, voids form below the film surface if diffusion is slow. Voids at the

interface with a refractive index of 1 would reduce the measured refractive index more drastically than would an oxide film in the thin film region. The outer low index film could be due to some surface oxidation of the nitride film or the adsorption of oxygen and/or moisture upon exposure to the room ambient. A thorough investigation of PECVD silicon nitride film profiles have been made using Fourier transform infrared spectroscopy, FTIR, Auger electron spectroscopy, AES, and X-ray photoelectron spectroscopy, XPS (14). FTIR showed an oxygen content near the interface which is due to either a native oxide or contamination. AES showed that near the interface silicon decreases abruptly while oxygen is found to increase. For thicker  $\text{Si}_3\text{N}_4$  films, AES show a Si rich layer within the silicon nitride near the surface. However, the excess silicon possibly as cluster was intentional (14). Our results do not show an increase in the index in the thick film region.

In order to quantify the relative decrease in the refractive index due to a low index interlayer or outer layer, 5 and 10 nm  $\text{SiO}_2$  films were purposely grown prior to the LPCVD nitride film deposition. The results in Fig. 3 show that samples with larger buried oxide layer yield lower index profiles and the resulting profile is sharper with decreasing nitride thickness. One finds reasonable agreement when the 5 and 10 nm oxide interlayer samples are modelled with 5.5 and 10.5 nm oxide films respectively as shown by the dash lines through the solid data points. The dashed line model curves in Fig. 3 are obtained from  $\Delta$ ,  $\Psi$  values calculated from a two layer model of an  $\text{SiO}_2$  film under a  $\text{Si}_3\text{N}_4$  film of varying thickness. The  $\Delta$ ,  $\Psi$  values are then used for the calculation of  $N_f$  using a one film model. The LPCVD nitride film with no purposely grown oxide (open circles) could be

modelled using a 4.5 nm inner oxide layer with an index of 1.465. However, this thickness is unreasonably high for a native oxide thickness. Alternatively, if one considers that the surface of the nitride film is slightly oxidized then a more reasonable model with 1 nm inner(i) and outer(o) oxide yield an excellent fit to the data(dashed line). It is important to note that the inclusion of an oxide film on top of the nitride film, lowers the composite refractive index more drastically as the nitride thickness decreases, than the identical oxide beneath the nitride film. Thus, one needs to include only a small amount of surface oxide to effect large changes in the composite film index. While we can not prove this assertion in the present study a more reasonable model is obtained using a surface oxide.

#### **As-Grown and Etch-Back Films**

A comparison of as-grown and the etch-back dry grown thermal  $\text{SiO}_2$  films is shown in Fig. 4. Both as-grown and etch-back oxides show an increase in  $N_f$  as thickness decreases verifying the notion that a higher index interlayer is present under  $\text{SiO}_2$  films as was presented above. The etch-back  $N_f$  profile, however, is consistently higher than the as-grown profile. This result appears to correlate with the previously reported intrinsic stress comparison (10) of as-grown vs. etch-back  $\text{SiO}_2$  films in which intrinsic stresses for etch-back oxides were found to be as high, if not slightly higher, than for the as-grown films. The simple viscoelastic model was found to be insufficient to explain this result (10). Using a simple Maxwell model for the  $\text{SiO}_2$  film, it is expected that since the thin as-grown oxides are exposed to high temperature for shorter times, these oxides should relax

less and should therefore display a higher stress and index than that obtained from etch-back samples which is in contradiction to past (10) and present results. It was suggested (10) that a more complex viscoelastic relaxation model is operative. Based on our present results we now believe that the effect of the chemical thinning and exposure to water needs to be considered to explain the results in Fig. 4.

First, Fig. 5 shows the  $N_f$  profile of  $\text{SiO}_2$  films grown in dry  $\text{O}_2$  at  $1000^\circ\text{C}$  and subsequently exposed to  $\text{H}_2\text{O}$  during the water rinse. Although only the  $1000^\circ\text{C}$  oxidation results are shown, the same behavior is observed for all etch-back  $\text{SiO}_2$  samples. The samples compared in Fig. 5 are first cleaned and oxidized simultaneously in the same oxidation furnace, and both films are etched back to various thicknesses and then thoroughly rinse with DI water. "Wet" oxide samples are ellipsometrically measured immediately after a thorough blow dry in  $\text{N}_2$  gas and "dry" oxide samples after being blown dry are stored in a dry  $\text{N}_2$  purged box overnight before measuring. The  $\text{SiO}_2$  films shown in Fig. 1 are of the "dry" oxide type. Fig. 5 shows that the water rinse has a profound effect on the film  $N_f$  with the "wet" oxide index consistently lower than the "dry" oxide index and with the deviation in  $N_f$  for the "wet" oxide growing larger with decreasing film thickness down to about 20 nm where  $N_f$  increases as was observed for "dry" films in Fig. 1 and 5. In the thin film region both the water and interface effects are present with the water effect which lowers the index being more pronounced near 20 nm and the interface effect dominating the thinner films.

In order to elucidate the interaction of the HF solution and/or water with the  $\text{SiO}_2$  films, we performed the following experiment with the results in Table 1. Two Si wafers were oxidized to about 70 nm at  $1000^\circ\text{C}$ , which is a thickness region where the index can be measured accurately to  $\pm 0.001$ . Treatment 1, oxide growth, shows an index for samples A and B to be the same. Both samples, A and B, were then immersed in water for one half hour, blown dry in  $\text{N}_2$  and then measured to see only the effect of water labelled as "wet" in Treatment 2 and yielding the same index for A and B. Both samples were then placed in a  $\text{N}_2$  dry box overnight and remeasured yielding a lower index for both A and B. Only sample B was then etched with a buffered HF solution ( $50:1/\text{NH}_4\text{F}:\text{HF}$ ) for 10 seconds and then followed by a thorough DI water rinse. This treatment led to a decrease in the index for B. The purpose of Treatment 3 was to isolate the effect of chemical etching and possibly residual chemical species and/or water. It is seen that storage in a dry box after etching increases the index. Then in Treatment 4 both sample were placed in an annealing furnace in dry  $\text{N}_2$  at  $200^\circ\text{C}$  for 5 minutes, in order to remove loosely bound water. Sample B decreased in index to its lowest value observed in the experiment while A, the un-etched sample remained unchanged. Finally, sample B was exposed to  $\text{H}_2\text{O}$  again in Treatment 5 yielded the highest index observed in this experiment. All the ellipsometric measurements from this experiment were made while the oxides were in a special box attached to the ellipsometer stage through which dry  $\text{N}_2$  flowed, thereby, minimizing contamination during measurement.

In an attempt to explain the water and HF effects in Table 1, a model for the effects on  $\text{SiO}_2$  film was constructed and shown in a series of cartoons in Fig. 6. First, we consider the amorphous  $\text{SiO}_2$  to be "porous" in the sense that there are pores and voids throughout the bulk and surface of the film as shown in Fig. 6a and significant evidence for this exists (16-19), although possibly not as depicted in 6a. At high temperature ( $>850^\circ\text{C}$ ) it has been shown that water may diffuse in fused silica either as the molecule or dissociated (20). However, at room temperature where our experiment was carried out, the water is likely to be only at the surface, and in the pores and voids, as is illustrated in Fig. 6b with the shading in the pores and voids. The result is an increase by .003 in the index of refraction because the pores and voids which have a refractive index of 1 when filled with water molecules display an increase in the index toward 1.33 thus resulting in a higher total index for the film depending on the portion of the voids affected.

In order to quantify the change in the index of refraction of oxide film, we used the Lorentz-Lorentz formula, (L-L) which relates the optical index to the film density and given as:

$$\frac{N_f^2 - 1}{N_f^2 + 2} = (4/3) \pi \sum N_j a_j \quad (1)$$

where  $N_j$  is the number of molecules per unit volume of component  $j$  and  $a_j$  is the electronic polarizability of component  $j$ . This formula is also known as the Clausius-Mossotti equation when  $N_f^2 = \epsilon$  is used. With the introduction of water into the oxide

we alter equation (1), in order to account of the permanent dipole moment,  $\mu$ , of water and obtain the Debye equation:

$$\frac{N_f^2 - 1}{N_f^2 + 2} = (4/3) \pi \sum N_j a_j + \frac{\sum \mu_j^2 N_j}{9 \epsilon k T} \quad (2)$$

Using equation (2), an increase in the index of .003 yields about .056% of water molecules in the oxide. Thus less than 1 part (water) per 1000 is needed to increase the total index of the film by .003 as was observed in step 2 for both samples. When sample B was etched and rinsed,  $N_f$  decreased below the original oxide index. Thus it is likely that the HF etching process enlarges the pores and voids on the surface of oxide, thereby enabling more water molecules of index of 1.33 to replace the original  $\text{SiO}_2$  of index of 1.465, hence lowering the overall index by .003 in the "wet" oxide. If this was true, then a still lower index would be obtained if the water molecules in the enlarged openings in the etched  $\text{SiO}_2$  film are replace with air. Indeed, we observed the lowest index in the case of annealed oxide in Treatment 4. Sample A is also annealed to assure that the change in index of oxide film is not due to annealing process but rather the removal of  $\text{H}_2\text{O}$  from surface voids. The decrease in  $N_f$  after annealing, Treatment 4, is -.006 and this corresponds to both the removal of about 1% of total of  $\text{SiO}_2$  that has been etched out by Treatment 3 plus the water removed by Treatment 4.

While the simple pore-void  $\text{SiO}_2$  film surface model, has some success in explaining the water and etching effect on the  $\text{SiO}_2$  refractive index the model is

incomplete. In particular the higher index for "dry" oxides after Treatment 3 and 5 is consistent with earlier etch-back data in Fig 4 but not with the simple model proposed herein. Further work is required and it is possible that residual chemical species of HF and contaminants from room ambient and water on the surface of these oxides can influence the  $N_f$  and are unaccounted for at this time.

A comparison of "wet" and "dry" nitride films prepared by PECVD is shown in Fig. 7. The refractive index of the "wet" nitride films is consistently higher than the "dry" films which is opposite to the oxide behavior shown in Fig. 5 but consistent with the oxide behavior in the proposed pore-void model. The proposed "porous" film surface model explains the result where air with an index of 1 replaces water with an index of 1.33 for the "dry" nitride film thus lowering the overall index.

Similar behavior for wet grown oxide is observed and shown in Fig. 8 in which all measurements on wet oxidized films are obtained from as-grown samples, therefore, eliminating any further water or etchant contamination at the oxide surface as in the case of "wet" oxide data presented above. It is therefore likely that any unusual deviation of the index profile would be due to the water interacting with the silicon or silicon dioxide during the oxidation. The presence of small amount of water has been known to enhance the growth rate of an oxide (21). The intrinsic stress (22) and refractive index (23) of wet grown oxides have been shown to be lower than the dry oxides. In our experiment the index of wet oxide is found to be consistently lower than the dry oxide in the thin film regime. This suggests that the "water" likely resides close to the interface.

### Conclusions

This study demonstrated that with appropriate algorithms and data handling procedures, reliable and useful information such as refractive index may be obtained from the ellipsometric measurement on very thin dielectric films. Higher index values are observed in the thin film region for  $\text{SiO}_2$  film prepared by both thermal and CVD processes indicating an oxidation interaction at Si-SiO<sub>2</sub> interface. CVD  $\text{Si}_3\text{N}_4$  on Si show a decrease in index at low thickness suggesting that native oxide or oxygen contamination may be present before or during the CVD process. A comparison of etch-back and as-grown oxides suggests complex behavior due to chemical and  $\text{H}_2\text{O}$  effect on the film surface. Index profiles for the wet grown thermal oxide indicates the possible existence of "water" near the interface.

### Acknowledgement

The research was supported in part by the Office of Naval Research, ONR and Northern Telecom Electronics Ltd.

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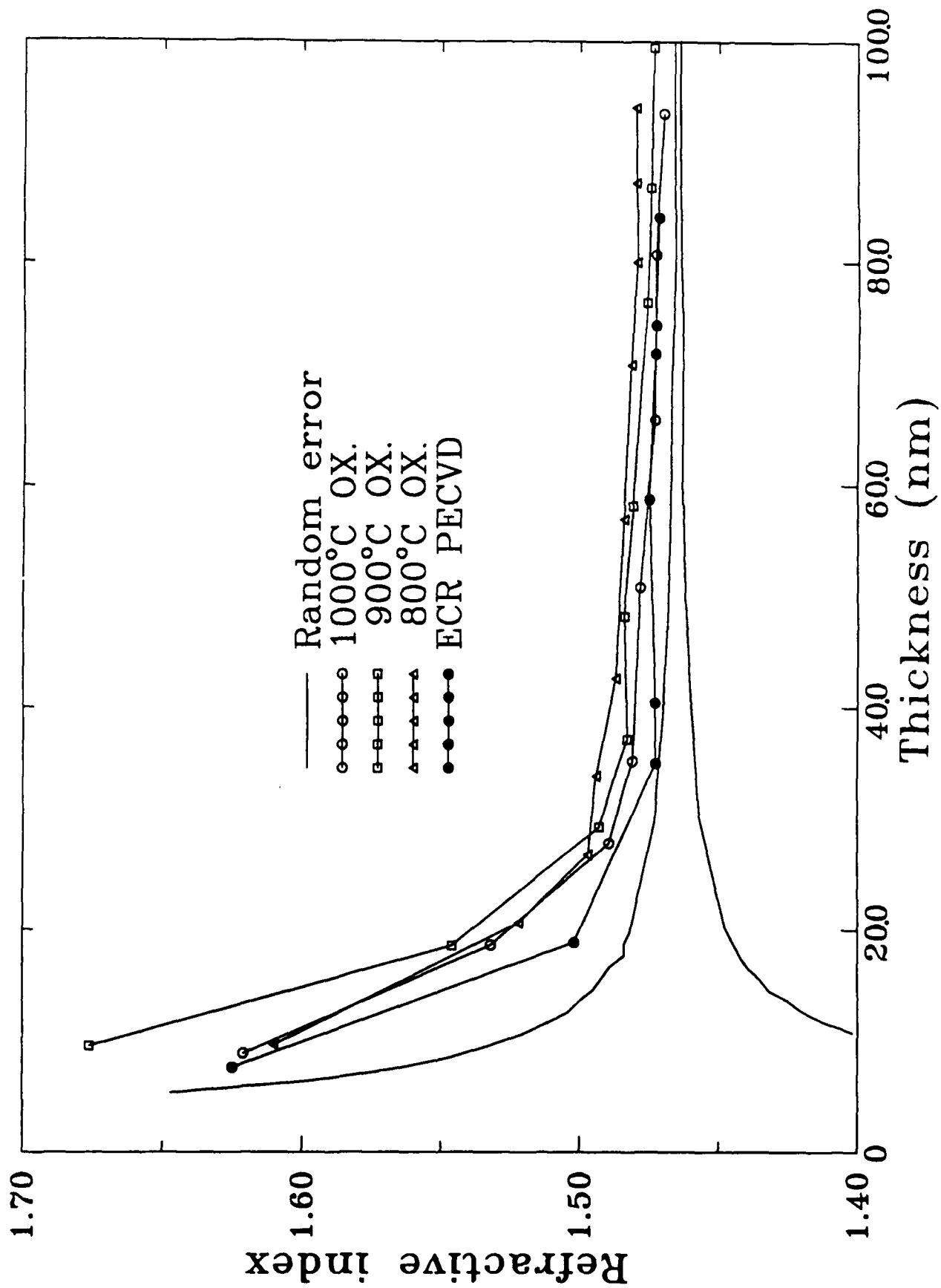
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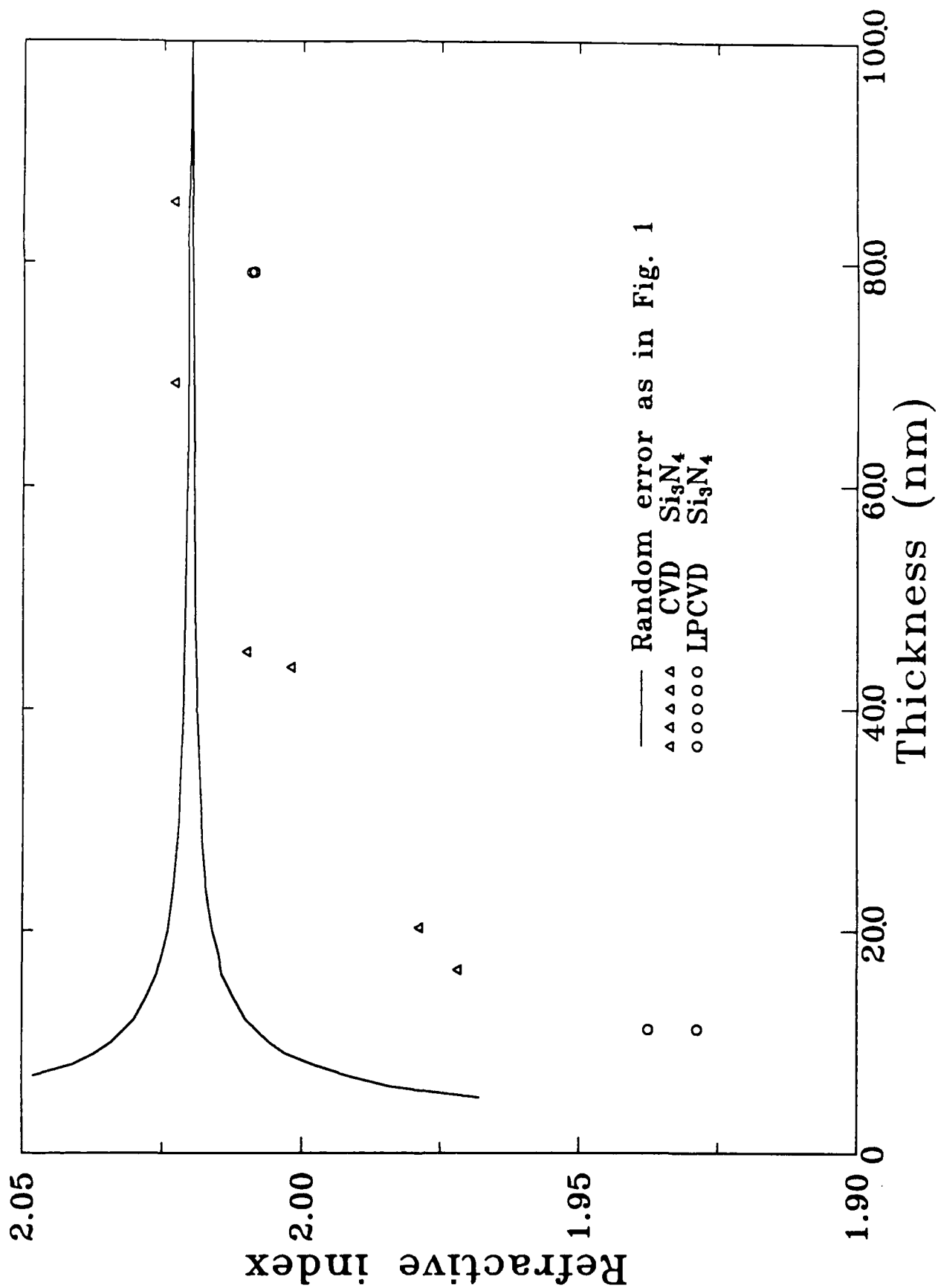
- Fig. 1. Experimental refractive index measurements on differently prepared  $\text{SiO}_2$  films along with the random error envelope.
- Fig. 2. Experimental refractive index measurements on LPCVD and PECVD  $\text{Si}_3\text{N}_4$  films along with the random error envelope.
- Fig. 3. LPCVD  $\text{Si}_3\text{N}_4$  films on intentional thermally grown  $\text{SiO}_2$  and with no intentional oxide. The dashed lines labeled 5.5 and 10.5 nm oxide are models using an inner oxide of the specified thickness. The topmost dashed line considers both an inner, i, and outer, o, 1 nm oxide.
- Fig. 4. Comparison of the  $N_f$  profiles for as-grown and etch-back samples for 1000°C dry thermal oxidation of  $\text{SiO}_2$  films.
- Fig. 5. Comparison of "wet" and "dry" etch-back  $\text{SiO}_2$  film.
- Fig. 6. A model for porous  $\text{SiO}_2$  films: (a) pores are shown on the surface and in the bulk; (b) surface pores are shaded to show filling by  $\text{H}_2\text{O}$ .
- Fig. 7. Comparison of "wet" and "dry" etch-back PECVD  $\text{Si}_3\text{N}_4$  films.
- Fig. 8. Comparison of wet and dry as-grown thermal oxidation at 800°C.

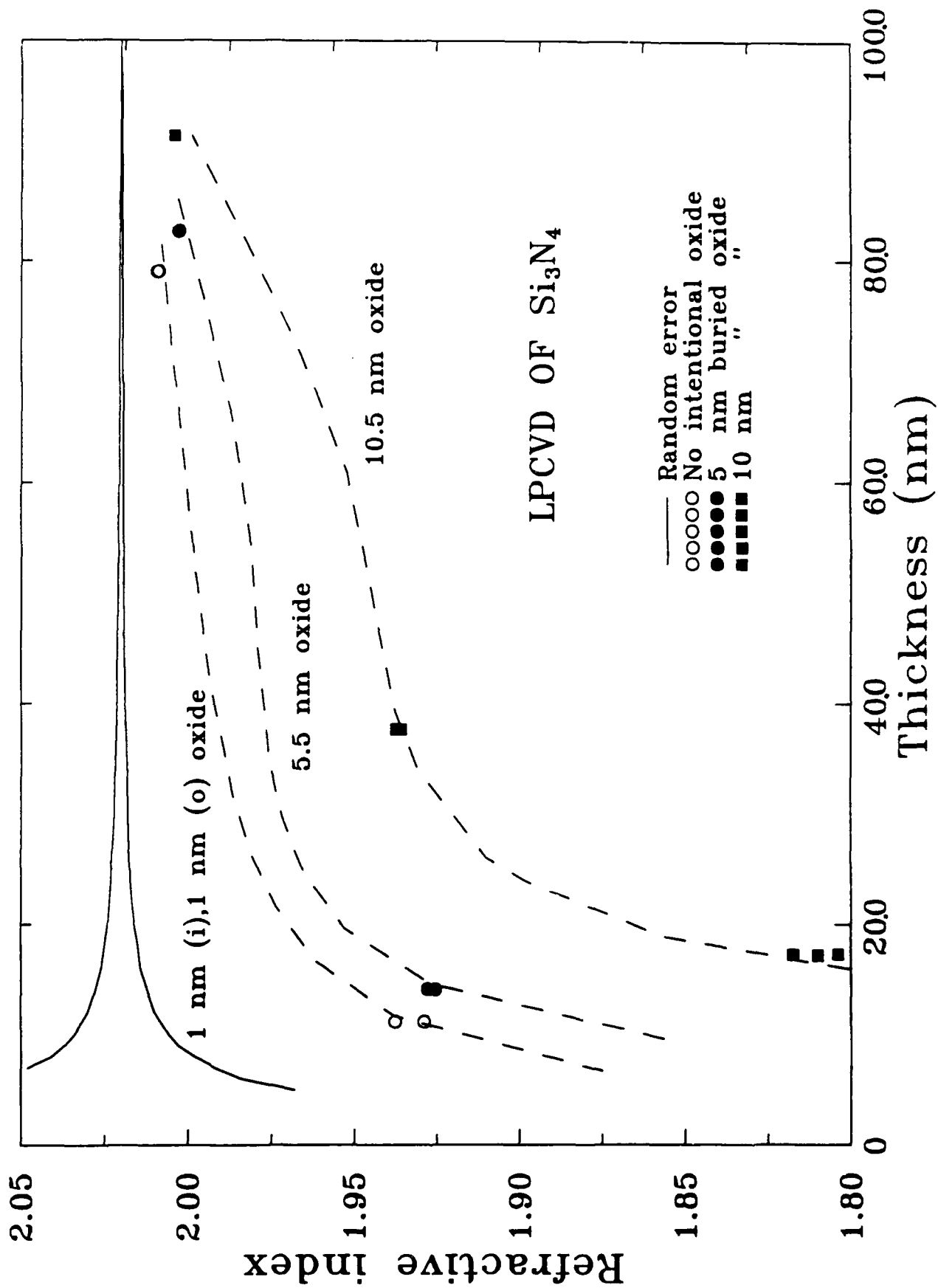
Table 1

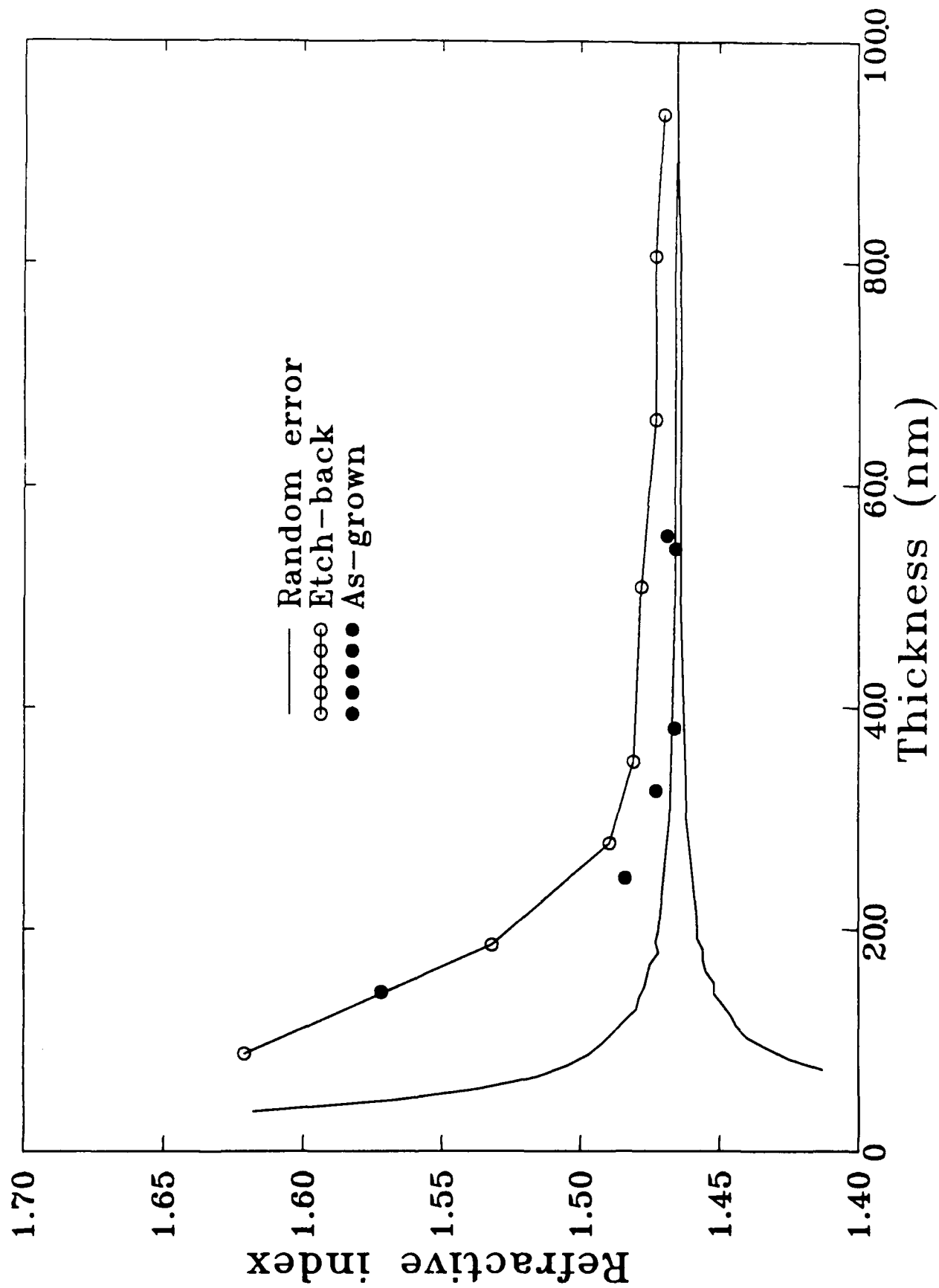
| Treatment                                      | Sample A    |              | Sample B |              |
|------------------------------------------------|-------------|--------------|----------|--------------|
|                                                | $N_f$       | $\Delta N_f$ | $N_f$    | $\Delta N_f$ |
| 1 As-grown:<br>1000°C, 70nm dry O <sub>2</sub> | 1.464       | 0            | 1.465    | 0            |
| 2 Water dipped<br>"wet"                        | 1.467       | +0.003       | 1.468    | +0.003       |
| "dry"                                          | 1.464       | 0            | 1.465    | 0            |
| 3 HF dipped+water rinse<br>"wet"               |             |              | 1.462    | -0.003       |
| "dry"                                          |             |              | 1.466    | +0.001       |
| 4 Anneal at 200°C.<br>5 minutes                | 1.464±0.002 |              | 1.459    | -0.006       |
| 5 Water dipped<br>"wet"                        |             |              | 1.470    | +0.006       |
| "dry"                                          |             |              | 1.466    | +0.001       |

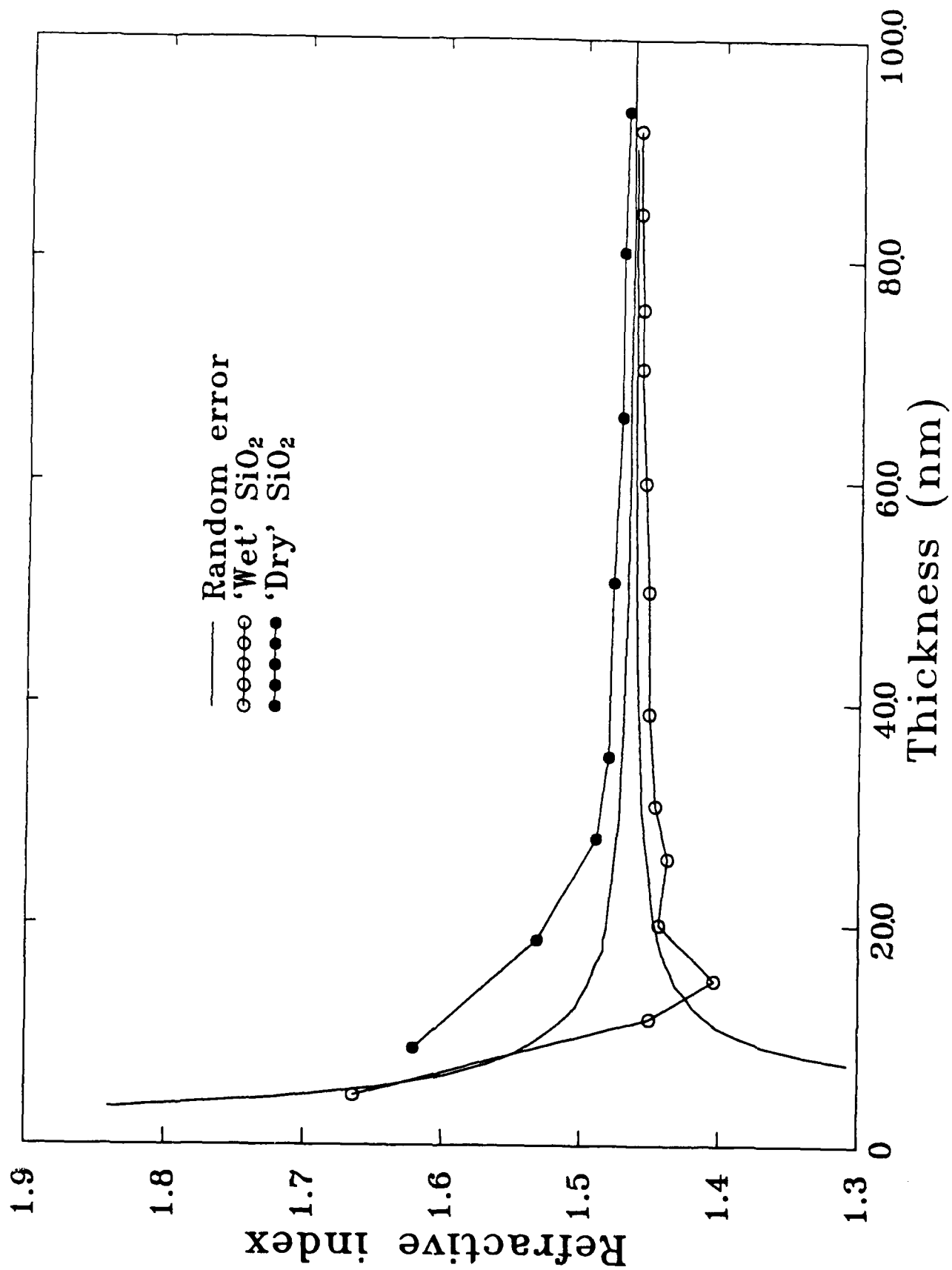
$$\Delta N_f = N_f - N_{as-grown}$$



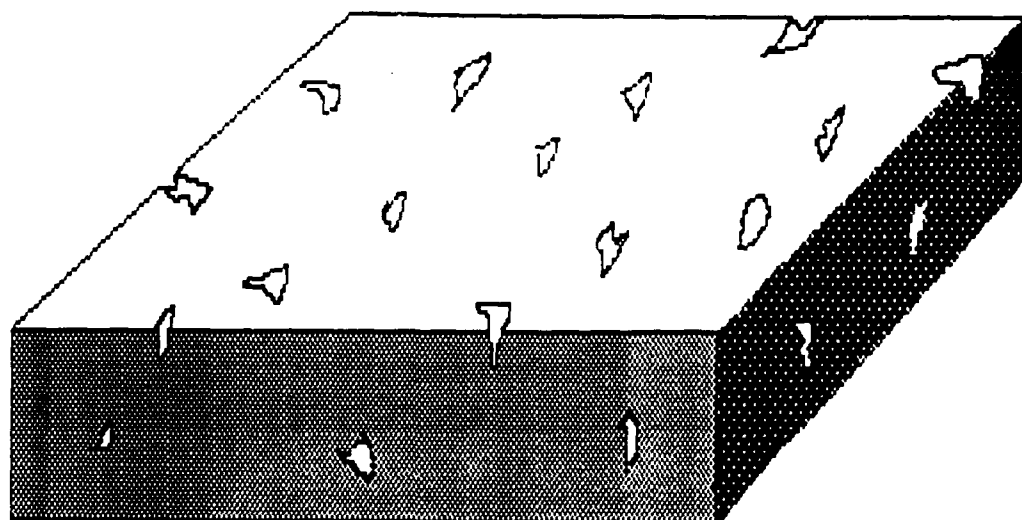








a)



b)

