TiSi-nitride attenuating phase-shift photomask for 193 nm lithography

Gillian A. M. Reynolds, R. H. French, P. F. Carcia, C. C. Torardi, Greg Hughes[‡], D. J. Jones, M. F. Lemon, M. Reilly, L. Wilson, C. R. Miao

DuPont Central Research & Development, Wilmington, DE 19880-0356
[‡]DuPont Photomasks, Inc., Round Rock, TX 78664

ABSTRACT

We have developed a new attenuating embedded phase-shift mask blank for 193 nm lithography based on novel TiSi-nitride chemistry. At 193 nm, these materials offer high optical transmission, they are radiation damage resistant, stable in common chemicals used to strip photoresist, process compatible with use of a hard Cr etch mask, and exhibit excellent dry etch selectivity to quartz. Specifically, optical transmissions of greater than 10% were achieved in films with 180^0 phase-shift. Irradiation at 6 mJ/cm^2/pulse, or ~60x the energy densities in commercial steppers, caused negligible change in optical transmission for doses up to 2 kJ/cm^2. Dry etching in an ICP reactor with CF_4+He or CHF_3+O_2 all gave greater than 6:1 etch selectivity to quartz, for optimized conditions. Further, the novel wavelength-tunable structure of these TiSi-nitride films permits equally attractive phase-shift designs at 248 nm and longer wavelengths. Currently, printing performance is under evaluation, and these properties will also be reported.

Keywords: Attenuating embedded phase-shifter, TiSi-nitride chemistry, 193 nm lithography

1. INTRODUCTION

As lithography moves towards the sub-0.18 micron generation, the wavelength restrictions and resulting materials demands require the use of innovative materials and technologies. The attenuating embedded phase-shift (APS) mask[1,2 ,3 4]technology has the ability of enhancing resolutions to sub-micron sizes in the 193 nm range. At these shorter wavelengths, however, only a few usable materials exist with band gaps greater than 6 eV.[5,6] In addition to this limiting feature, these materials also need to satisfy 11 lithographic properties: phase-shift, transmission and reflection at the lithographic wavelength, inspectability, etch selectivity to quartz and resist, chemical durability, radiation durability, film adhesion to quartz, and low film stress.

We have developed such a first generation material from a TiSi-nitride based chemistry with a phase-shift of 180^0 +/- 5^0 and a transmission of 9% ± 1.0. We report here on the performance of this novel material with respect to the criteria described above.

2. EXPERIMENTAL TECHNIQUES

The TiSi-nitride samples (DM1 material) used for this work were sputtered in a Perkin Elmer 2400 tool in Ar and N_2 atmospheres onto quartz substrates from 8" diameter targets. Film stresses were kept at a minimum by using gas pressures on the order of 10^{-2} mbar during sputtering.[7] Several post-deposition measurements were made to ensure consistency among and between batches of samples. The resulting attenuated phase-shift (APS) blanks (unpatterned) were physically characterized for thickness using a Dektak profilometer. Atomic force microscopy (Digital Instruments Nanoscope IIIa) was used to determine surface structure and roughness. A Perkin Elmer UV-Vis spectrophotometer was used to measure the reflection and transmission of films.

Ellipsometry measurements[8] were taken to determine the complex optical constants, spectral phase-shifts and film inhomogeneities. Samples (6" x 6") were mounted in a Woollam DUV ellipsometer equipped with MgF_2 polarizers and analyzers and capable of wavelengths from 186 to 1100 nm. The spot diameter at the sample is 2 mm. By translating the samples in the ellipsometry tool, a transmission map over a 14 x 14 cm^2 area (5.5" x 5.5") of the samples could be determined. These maps were then used to study any lateral inhomogeneities in the transmission properties of an APS blank.

Chemical durability tests were performed on films using aqueous solutions of CR7 chrome etchant ($Ce^{4+}/HClO_4$), H_2SO_4 (conc.), NH_4OH and Nano-Strip (H_2SO_4/H_2O_2) at ambient or elevated temperatures. For all the tests, samples were mounted in a Teflon rack such that the entire film could be immersed into test solutions. The test solutions were held in Pyrex straight-walled dishes. Heating of test solutions was done in a heating mantle operated by a digital temperature probe/controller. After

G. A. M. Reynolds, R. H. French, P. F. Carcia, C. C. Torardi, G. Hughes[‡], D. J. Jones, M. F. Lemon, M. Reilly, L. Wilson, C. R. Miao "TiSi-nitride attenuating phase-shift photomask for 193 nm lithography", **18th Annual BACUS Symposium on Photomask Technology and Management, SPIE Vol. 3546**, Edited by B. J. Grenon, F. E. Abboud, 514-23, (1998).

each test, samples were rinsed three times in clean deionized water, rinsed in methanol, and air dried. For Nano-Strip and H_2SO_4 cleaning, samples were soaked in 80^0C solutions for various cumulative soak times up to 120 minutes. For Cr wet etch (CR7) studies, samples were immersed into concentrated CR7 at ambient temperature for 20 minutes. For NH_4OH rinsing, samples were immersed in aqueous 7% NH_4OH at ambient temperature for 15 minutes then rinsed in a deionized water bath. Before the samples were characterized, they were cleaned by spraying with methanol, wiping with a lint-free cloth, rinsing with deionized water, and drying in a stream of nitrogen. Changes in the transmission from 180 to 800 nm were measured.

ICP etch tests were performed on 5” x 5” APS blanks using two etch gases: CF_4 + He and CHF_3 + O_2. Measurements were carried out at low pressures (5 mTorr) and at a medium power of 250 Watts. The variables of RIE power and diluting gas were studied. Low RIE powers of 5 Watts were used to enhance the chemical etching of the APS, while high RIE powers were used to characterize the etch rates under more anisotropic conditions. Etch rates of quartz were obtained using separate patterned Cr/Qz masks. These rates were obtained using fixed etch times of 4 minutes. A profilometer was used to measure the amount of quartz etched, after subtracting the starting Cr thickness.

To determine the life-time usage of the films, accelerated radiation durability tests were performed using a Lambda Physik Excimer laser running with ArF at 193 nm. Samples were mounted in an environmental cell, thus ensuring control over their atmosphere, be it nitrogen or air. The samples were radiated from the quartz side with fluences on the order of 6 mJ/cm^2/pulse at 100 Hz for doses up to 2 kJ. The radiation durability of the films were examined as functions of chemical composition, environment and laser dose. A Perkin Elmer spectrophotometer was used to determine the transmission and reflection from 180 to 800 nm before and after radiation exposure.

3. RESULTS AND DISCUSSION

If we consider using a fugitive mask process to make a photoblank there are various steps involved in the process, as shown in Figure 1. Current techniques for etching patterns involve chemicals such as CR7 and Nano-Strip. Thus, once a candidate material has been created, we need to know how it will perform under various etching processes. From chemical durability studies on two first generation (DM1) materials, it was found (see Figure 2 and Figure 3) that the films exhibit excellent durability ($(\%T_f - \%T_i)_{193} < 1.0$) when exposed to hot Nano-Strip and H_2SO_4 for up to 120 minutes (the equivalent of eight etch washes). Figure 4 shows the percent transmission as a function of wavelength after a 20 minute exposure to the CR7 chrome etchant. The etch durability was also favorable in this case, with $(\%T_f - \%T_i)_{193} < 0.6$. Table 1 shows eight films after a 15 minute exposure to 7% NH_4OH. Unlike films 9209-9210, films 9177-9180 were not previously exposed to Nano-Strip and H_2SO_4. The changes in transmission in the samples previously exposed to Nano-Strip and H_2SO_4 were negligible. The other four films had changes in transmission on the order of 0.2. These changes were comparable to those observed in films 9209 and 9210 after Nano-strip and H_2SO_4 exposure. These studies show that this new TiSi-nitride chemistry is chemically durable, making them compatible with current mask fabrication processes.

Preliminary dry etch studies on the new TiSi-nitride chemistry have also been done. Using CF_4 as the etch gas (see Figure 5) works well without the He diluent with the best etch ratios of APS to quartz (Qz) being obtained at low reactive ion etching (RIE) power. Although the etch rate for the APS does go up with increased RIE power the Qz etch rate goes up proportionately faster causing the ratio of the two to decrease. In general, the APS etches similarly for both gas cases but the Qz etches best in the CF_4. The results for the CHF_3 etch system are shown in Figure 6. Although some good etch ratios were obtained using this system it might be hard to establish a reliable point (low RIE) where Qz is not etched but where the APS is etched.

From the ellipsometry measurements, we have determined that the sputtered TiSi-nitride photoblanks have transmissions on the order of 9% +/- 1.0 at 193 nm and 40% at 248 nm (where future inspection tools are under development) with phase-shifts on the order of 180^0 +/- 5^0. We have also been able to configure photoblanks with 6% tranmission at 193 nm. Figure 7 plots the transmission versus photon energy of two photoblanks as measured using the ellipsometer tool. The transmission is seen to fall off steadily to ~9% at 6.45 eV (193 nm) in one photoblank and to ~6% in the other. Figure 8 shows that the corresponding transmission map at 193 nm for the 9% transmission photoblank exhibits uniform transmission over the large 6” x 6” surface. Figure 9 shows the corresponding plot of n (index of refraction) and k (extinction coefficient) versus energy. These n and k values were obtained from modeling the experimental reflectance and transmittance spectra of the films on a substrate.

For the accelerated radiation studies, the films were found to be durable up to doses of 2 kJ in flowing air. Films subjected to a nitrogen atmosphere were found to be more radiation durable than those radiated in flowing air. Table 2 shows the results of these environmental tests for films radiated at 100 Hz and an energy density of 6 mJ/cm^2/pulse for a 2 kJ dose. The changes in transmission $(\%T_f - \%T_i)_{193}$ in nitrogen were 0.4 as compared to 1.5 in air. Preliminary results from

marathon radiation durability studies (being conducted at Lincoln Labs by V. Liberman and M. Rothschild) show similar trends. The radiation durability of the films was also affected by their chemistry. By varying the chemical composition of the film, we were able to affect the amount by which the transmission changed after radiation exposure. This is shown in Figure 10 for films radiated in air at 100 Hz and 6 mJ/cm^2/pulse for a 2 kJ dose. Increases in the TiN content increase the radiation durability.

4. CONCLUSIONS

We have designed a new TiSi-nitride attenuated embedded phase-shift mask that is optically tunable for 193 and 248 nm lithography applications. The work to date has shown that this material is chemically durable to standard fugitive chrome and resist etching protocols, exhibits good etch selectivity to quartz, and is radiation durable for energy densities of 6 mJ/cm^2/pulse and doses up to 2 kJ.

5. ACKNOWLEDGMENTS

This work was sponsored in part by Sematech under project number LITG361. Collaborations with M. I. T. Lincoln Laboratory with Mordechai Rothschild, Vladimir Liberman and Roderick Kunz for marathon radiation durability testing and 193 nm lithographic printing is appreciated. The ICP Etching studies were performed Plasmatherm using a VersaLock ICP Etch Tool. .

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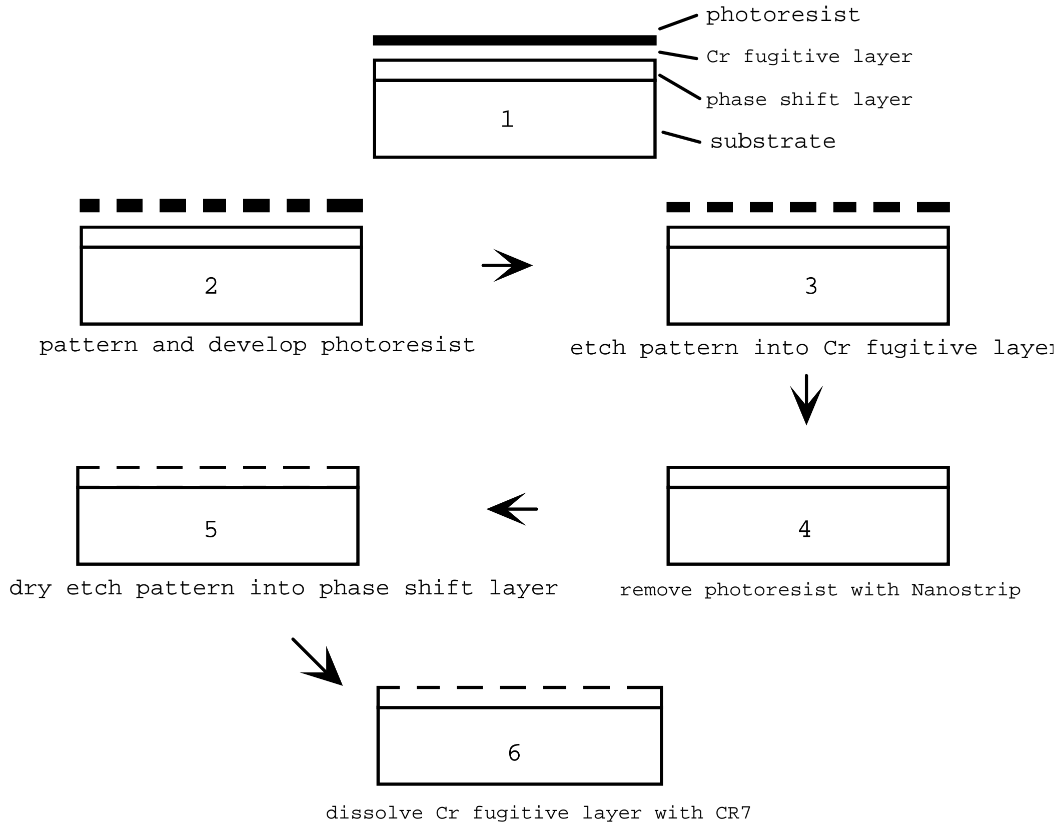

Figure 1 Showing the process of etching a pattern into the attenuated embedded phase-shift mask material. A variety of chemical processes are used for patterning and etching.

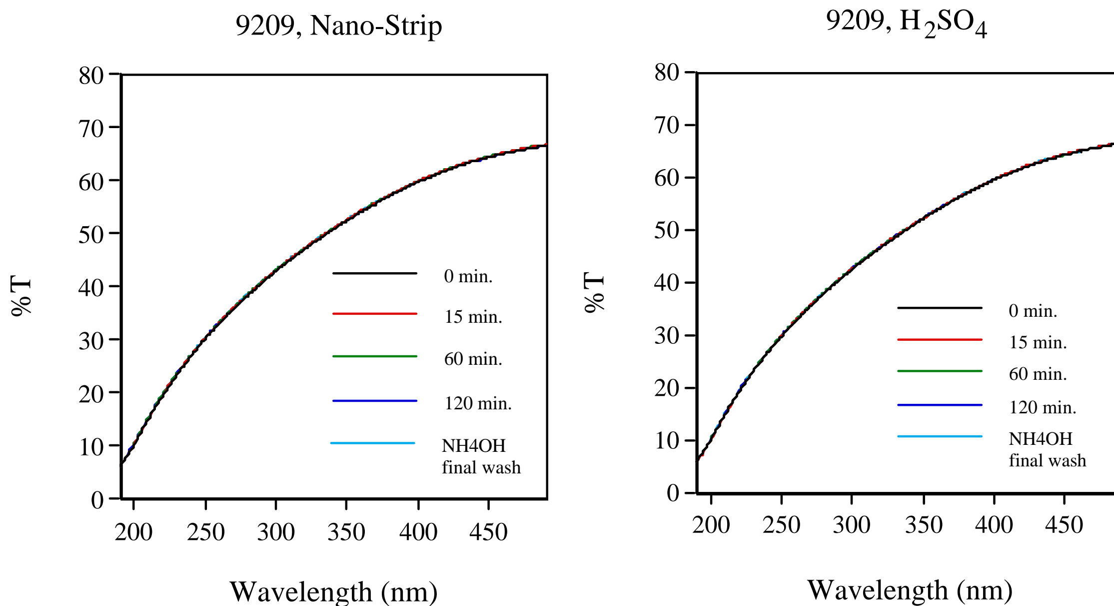

Figure 2 Showing the % transmission versus wavelength for sample 9209 before and after various timed exposures to hot Nano-Strip and H_2SO_4. Changes in transmission at 193 nm are less than 0.30. Spectrometer error in the transmission measurements is estimated to be ~0.03 in units of %T at 193 nm.

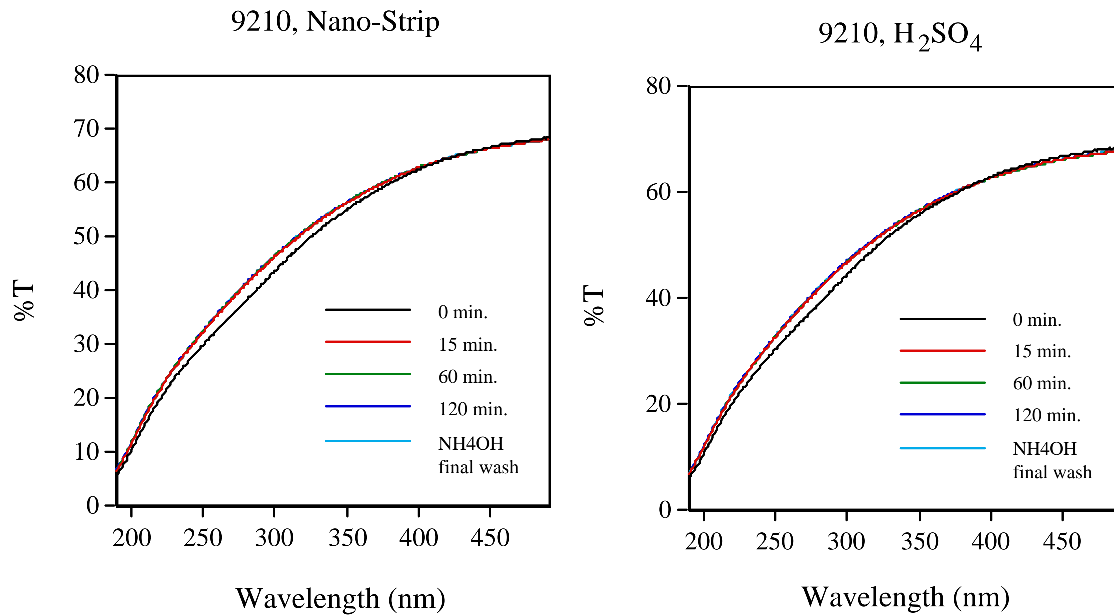

Figure 3 Showing the % transmission versus wavelength for sample 9210 before and after various timed exposures to hot Nano-Strip and H_2SO_4. The change in transmission at 193 nm is 1.0. Spectrometer error in the transmission measurements is estimated to be ~0.03 in units of %T at 193 nm.

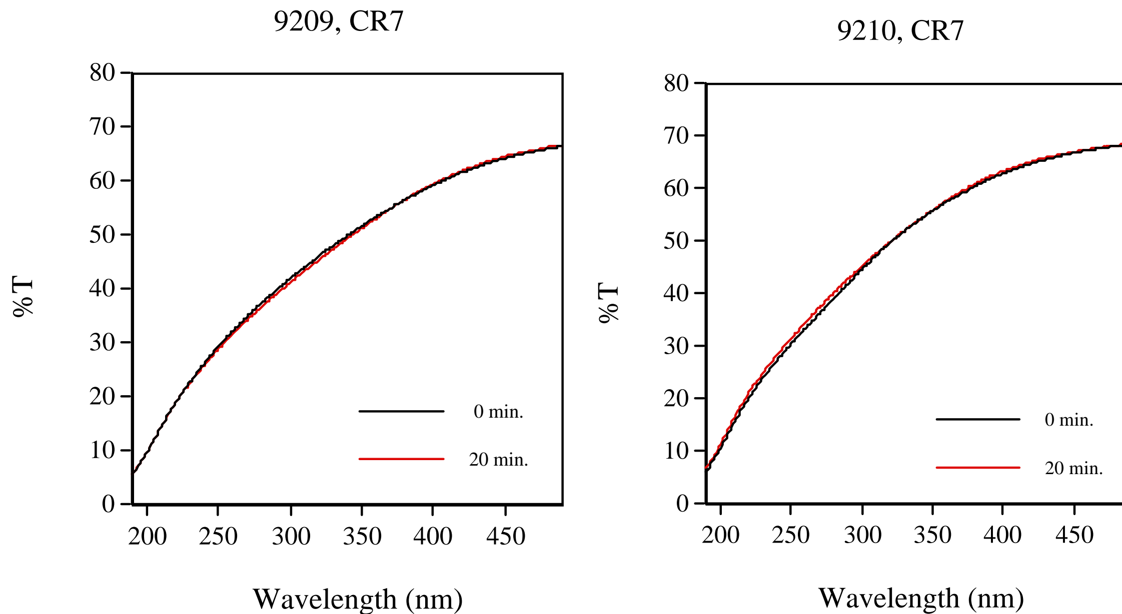

Figure 4 Showing the % transmission versus wavelength for samples 9209 and 9210 before and after a 20 minute exposure to CR7 chrome etchant. Changes in transmission at 193 nm are less than 0.6. Spectrometer error in the transmission measurements is estimated to be ~0.03 in units of %T at 193 nm.

Chemistry Number	%T (0)	%T (15)	Δ%T	Comments
9177	7.346	7.561	0.215	fresh DM1 samples
9178	12.233	12.565	0.332	fresh DM1 samples
9179	6.538	6.309	-0.229	fresh DM1 samples
9180	12.116	12.620	0.504	fresh DM1 samples
9209	7.401	7.355	-0.046	after 2 hr Nano-Strip soak
9209	7.255	7.269	0.014	after 2 hr H_2SO_4 soak
9210	8.016	7.990	-0.026	after 2 hr Nano-Strip soak
9210	8.301	8.343	0.042	after 2 hr H_2SO_4 soak

Table 1 Showing the % transmission at 193 nm of DM1 thin films before and after a 15 minute washing in 7% NH_4OH. Samples 9209 and 9210 underwent 2 hour soaks in H_2SO_4 and Nano-Strip before washing.

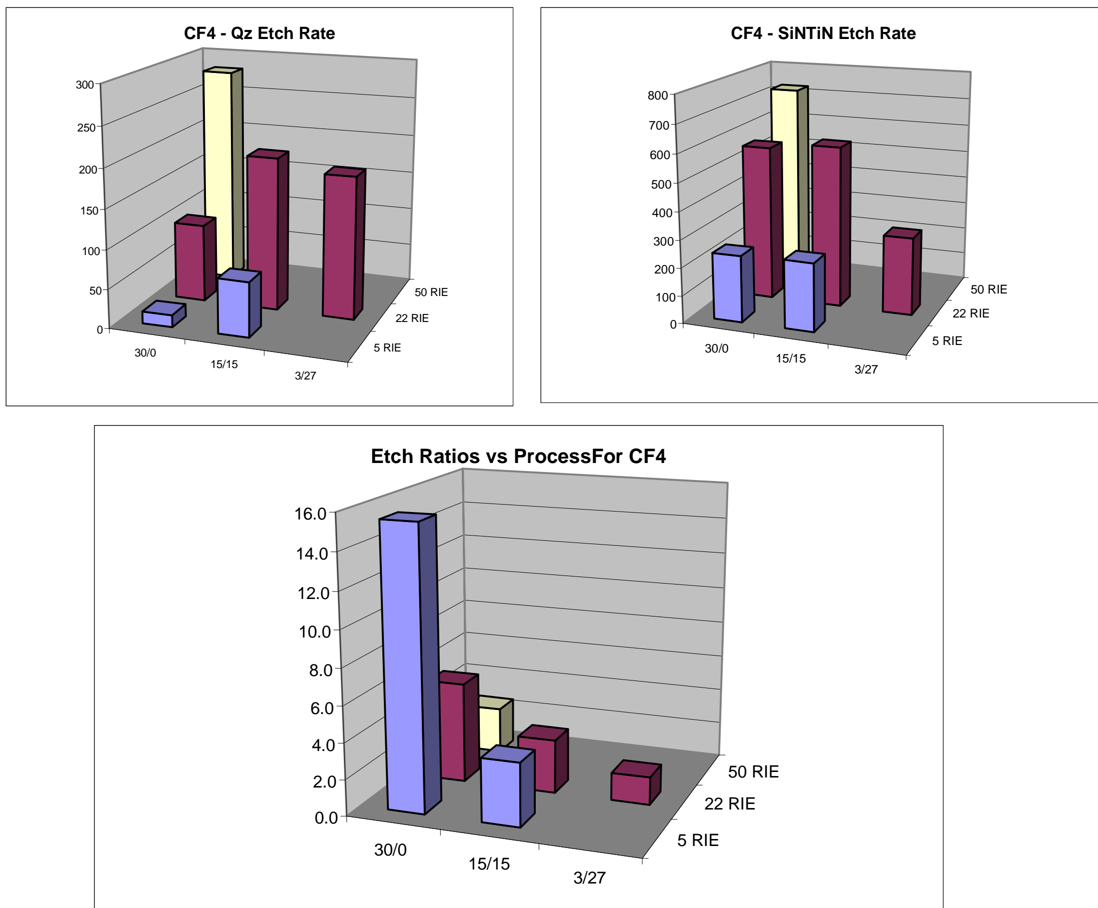

Figure 5 DM1 Photoblank Dry Etch Results for CF_4 etching.

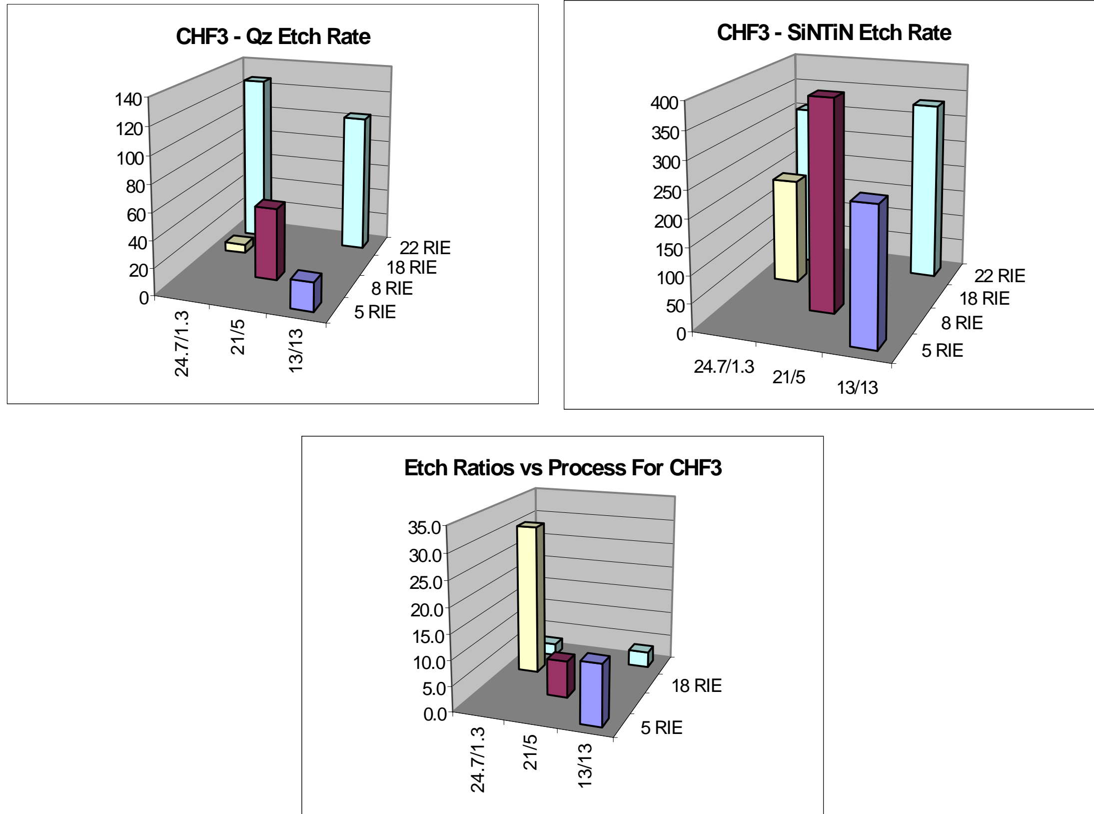

Figure 6 DM1 Photoblank Dry Etch Results for CHF_3 etching.

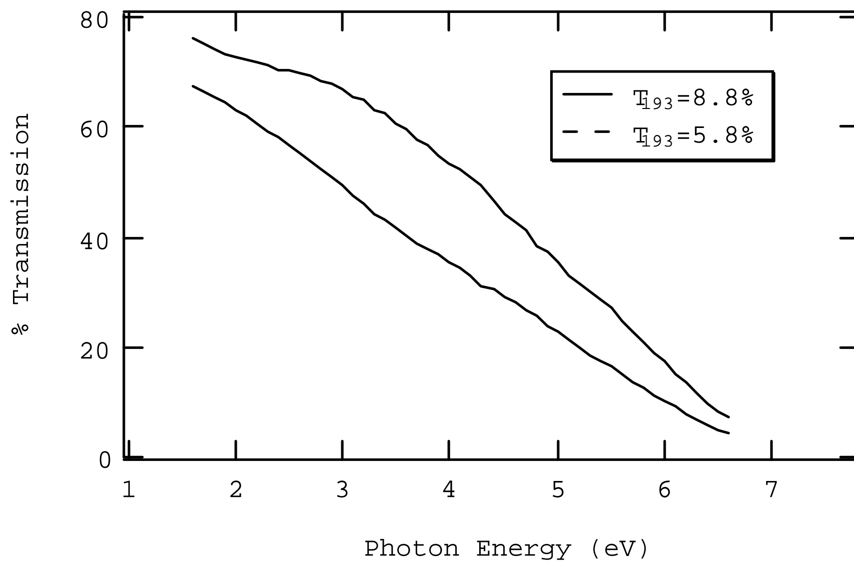

Figure 7 Showing transmission as a function of photon energy for materials with ~9% and ~6% transmission at 193 nm (6.45eV).

Figure 8 Showing the transmission map at 6.45 eV across the face of the photoblank material in the previous figure. The transmission is fairly uniform at ~8.8% across the sample.

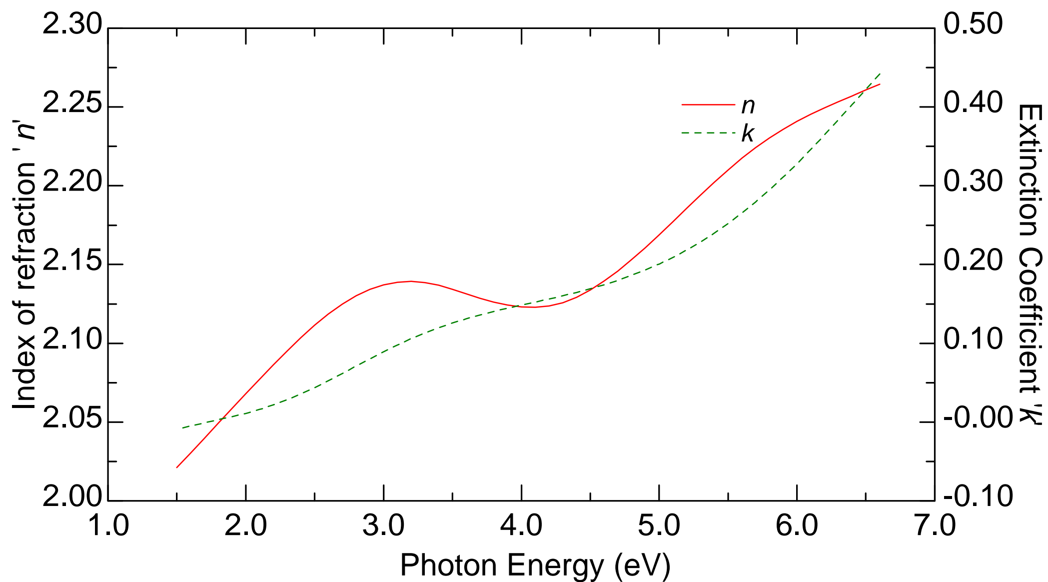

Figure 9 Showing the calculated index of refraction, *n*, and the extinction coefficient, *k*, versus photon energy corresponding to DM1 material 9235-18.

DM1 Sample #	Environment	%T (before)	%T (after)	Δ%T
9153-4	Air	9.3	10.8	1.5
9153-5	Nitrogen	9.6	10.0	0.4
9152-3	Air	13.3	16.1	2.8
9152-4	Nitrogen	14.0	16.9	2.9

Table 2 Listing % transmission at 193 nm before and after radiation as a function of environment for DM1 films 9153 and another candidate material (9152). The samples were radiated at 100 Hz and an energy density of 6 mJ/cm^2/pulse for a 2 kJ dose.

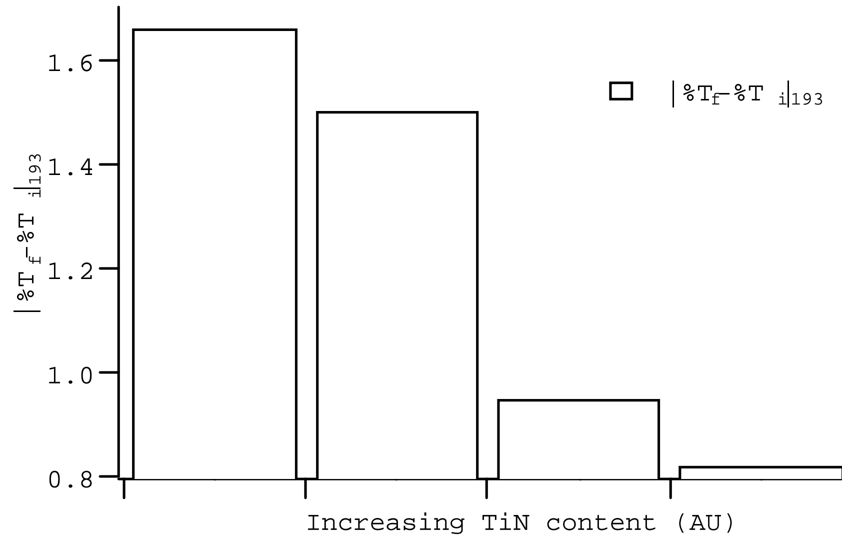

Figure 10 Showing the effects of chemical composition on transmission changes. Samples were radiated in air at 100 Hz and an energy density of 6 mJ/cm^2/pulse for a 2 kJ dose.