

Relation between Local Composition, Chemical Environment and Phase Shift Behavior in Cr-Based Oxycarbonitride Thin Films

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ABSTRACT:

The latest deep ultra-violet (DUV) photomask technology requires macroscopic properties such as optical transmission, reflectance, and chemical reactivity to be precisely controlled. Therefore, a fundamental understanding of the relationship between atomic bonding and nanometer scale property variation is required. Thin films of Cr-O-C-N are compositionally graded to produce specific attenuation and phase shift of optical radiation. A combination of techniques was used to relate the local atomic bonding to macroscopic properties. Sputtered neutral mass spectroscopy was used to resolve local composition, and variable angle spectroscopic ellipsometry was used to determine local optical properties (on nm scale) that are then related to local composition. Core level shifts in X-ray photoelectron spectroscopy characterize changes in the Cr environment associated with changes in composition. A model is suggested in which bonding at the atomic level is controlled within different 10-100 nm sized regions which can be combined to produce arbitrary optical properties.

INTRODUCTION

The minimum feature size in state of the art integrated circuitry steadily decreases with time. Techniques of lithographic production need to evolve to meet this demand. The most conceptually simple method is to decrease the wavelength of the incident radiation used in patterning. In recent years, patterning wavelength has decreased with feature size from 488 nm, 365 nm, 248 nm to 157 nm. In traditional binary image mask lithography, incident wavelength limits minimum feature size due to diffraction broadening. Phase-shifting photolithography effectively combats this problem. Phase shifting photomasks allow the possibility of "sub-resolution" lithography - 157 nm radiation can be used to print features as small as 80 nm with phase shifting photomasks.

Optical lithography might also prove useful in new fabrication schemes, for example in conjunction with self assembly in the patterning of organic materials. This process requires substantial wavelength flexibility. Solutions for phase shifting/wave guide technology developed for traditional optical lithography will facilitate engineering on the nanometer scale.

Controlling phase shift and transmission at a variety of wavelengths is currently done empirically. Understanding the fundamental relationship between bonding and optical properties in phase shifting photomask films would yield a strategy for developing new masks for emerging nanofabrication needs. This is the goal of the present work using a combination of XPS, EELS, SNMS and ellipsometric results on production-grade CrOCN phase-shifting photomask films designed for 180° phase shift and 5-10% transmission at prescribed incident wavelength.

EXPERIMENTAL PROCEDURES

Three CrOCN films in which composition gradients result in a 180 degree phase shift and controlled transmission of 248 nm, 365 nm, and 436 nm incident light are the subject of this study as well as a fourth non-shifting CrOCN film. The sample films are referred to by their operating wavelength (i.e., the film used to shift and attenuate 248 nm light is referred to as a “248 nm film”) with the exception of the non-shifting film which will be referred to as “COQ,” short for traditional “chrome on quartz” opaque photomask. Each of the four films were made using reactive sputter deposition from Cr targets in N₂, O₂, CO₂, CH₄, and Ar at a total pressure of the order of 10⁻³ Torr. Varying the gas composition during the deposition varies the local composition of the film, yielding the compositional gradation with depth necessary for the phase shift. This process has been described in detail in previous work¹.

Film chemical composition profiles were acquired through Sputtered Neutral Mass Spectroscopy (SNMS) and have been presented previously¹. Cr coordination was determined with a statistical analysis of this composition data as outlined in reference 1. X-ray Photoelectron Spectroscopy (XPS) was carried out in a PHI 5400 ESCA system using non-monochromatic Mg-K_α radiation. The XPS system was equipped with a concentric hemispherical analyzer operated at constant pass energy. The energy scale of the analyzer was calibrated using the Ag 3d_{5/2} peak set at 368.3 eV. XPS spectra of the C 1s, N 1s, O 1s and Cr 2p energy regions were measured at a detection angle of 45°. Since Auger electron spectroscopy and SNMS verified the presence of 2-5 nm of surface contamination, electron binding energies were not acquired with XPS before removal of this contamination layer by sputtering with 3 keV Ar⁺ ions and the intensity of the carbon peak attained the bulk value in each film. Optical properties were measured with Variable Angle Spectral Ellipsometry (VASE) as described in detail in reference².

RESULTS and DISCUSSION.

An example SNMS chemical depth profile of one of the films appears in Figure 1. These films are laterally chemically homogeneous and the optical properties are extraordinarily sensitive to overall composition¹.

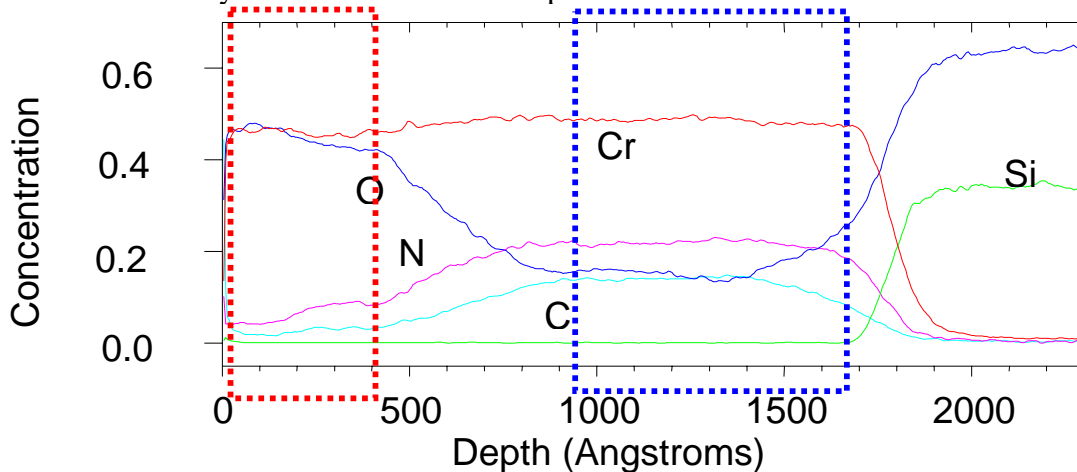


Figure 1. Composition profiles from sputtered neutrals mass spectroscopy showing composition gradients for an example CrOCN thin film (488 nm film). The regions outlined are defined as ‘nearly constant’ compositions and 10-50 compositions within such a region have been used for statistical analysis.

X-ray diffraction reveals that the film structures lack long-range order³. Note that the 40 nm of the film closest to the surface layer as well as the 70 nm closest to the SiO₂ interface (the two boxed regions in the figure) are regions of relatively constant composition.

The results of the statistical analysis of the SNMS data for all films are printed in Table I.

Table I Results of Statistical Analysis of the SNMS data.

Operating λ (nm)	Thickness (Å)	Film region	[O]	[N]	[C]	[Cr]	a	b	c
coq	1029.00	Top	0.32	0.19	0.06	0.43	0.82±0.15	5.64±1.00	9.91±1.02
		Bottom	0.01	0.23	0.05	0.71	0.02±0.05	1.12±0.53	9.30±0.43
488	1257.00	Top	0.44	0.07	0.03	0.46	1.02±0.05	2.74±0.31	9.85±0.36
		Bottom	0.15	0.22	0.14	0.49	0.37±0.15	3.12±0.18	9.90±0.25
365	1082.00	Top	0.48	0.06	0.02	0.43	1.17±0.05	3.39±0.09	9.89±0.22
		Bottom	0.19	0.22	0.14	0.45	0.47±0.05	6.93±0.24	9.99±0.29
248	1109.00	Top	0.56	0.03	0.01	0.41	1.42±0.05	2.05±0.12	9.97±0.04
		Bottom	0.40	0.13	0.03	0.44	0.97±0.05	5.28±0.26	9.98±0.34

The goal of the analysis is to determine if stable compositions imply several discrete coordinations of the various anions in the system with Cr. The procedure has been described in reference 1 and the anion/cation atomic ratios resulting from the analysis are summarized in Table I. The parameter 'a' is the best fit oxygen coordination to Cr whereas, the best fit N and C coordinations with Cr are 'b' and 'c', respectively. Since C is present at rather low levels and is less reactive with Cr, it is considered an impurity. Note that the fit oxygen coordinations correspond well to either Cr₂O₃ (a ~ 1.5), CrO (1.0) or a mixture of the two (1.33). Since the mathematical regression was unbiased with respect to these bonding configurations, this result indicates that the species in these films adopt local coordinations that occur in crystalline solids.

In some cases in the above table, the Cr-anion coordinations that fit the SNMS data do not correspond to valences commonly found in binary compounds. As reported previously, we have discovered a regime that might account for this variation using ternary compounds¹.

XPS spectra of the Cr 2p peak are presented in Figure 2. These spectra were obtained in the relatively chemically homogeneous film regions of each film near the surface and film/substrate interface (boxed regions in figure 1). As some of the films were insulating some effects of sample charging were observed in the data. However, the positions of the Cr 2p peaks in the spectra were observed to change significantly with respect to the N 1s and the O 1s peaks. Given that oxygen is highly electronegative, it can be assumed not to change valence in these samples. Thus, oxygen is assumed to be present as the O²⁻ ion. Then, in order to define a universal energy scale we have chosen to use the O 1s binding energy as a reference. All spectra displayed in Figure 2 have been shifted so that the O 1s peak occurs at 530.2 eV, close to its value in Cr₂O₃⁴.

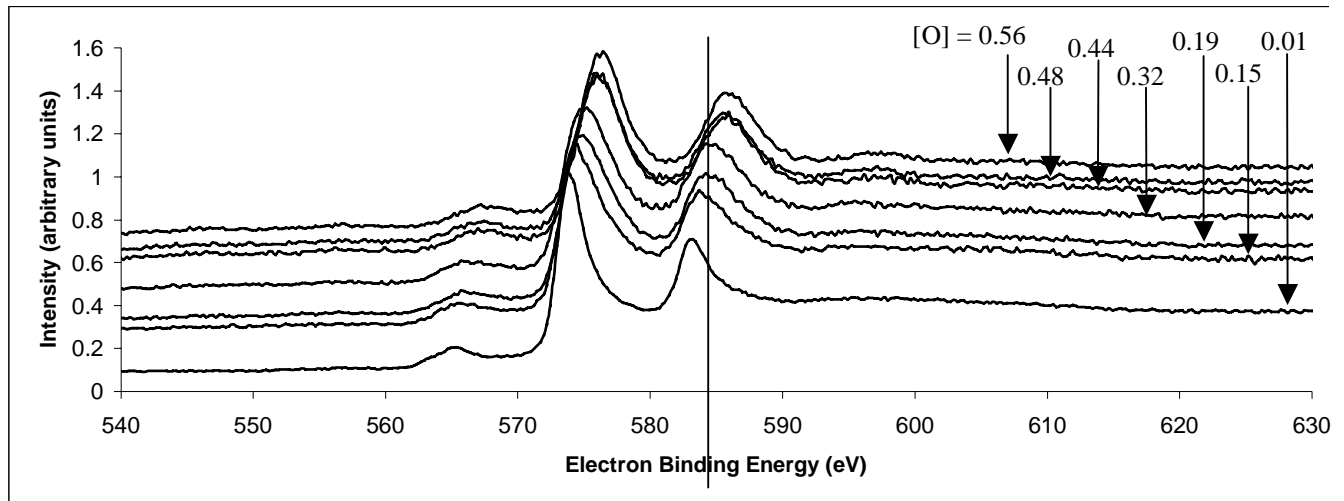


Figure 2. Cr 2p peak shift for all films in study. The spectra are labeled according to the oxygen concentration of the specimen.

As implied above, the location of the Cr 2p_{1/2} and 2p_{3/2} peaks with respect to O 1s do change significantly from sample to sample. This is reflected in the data displayed in Figure 2. Note that both Cr 2p peaks trend toward higher energy with increasing oxygen concentration. This indicates a continuous change in the chemical environment of Cr in these samples with oxygen content. The trend may indicate an increase in Cr valence with increasing oxygen concentration. This is consistent with earlier results from electron energy loss spectroscopy (EELS)¹ which showed an increase in d orbital occupancy with oxygen concentration for at least one film.

Spectrally resolved ellipsometry data for an example film appears in Figure 3. From analysis of the ellipsometric data the refractive index and extinction coefficient (a measure of absorption) for the 10-100 nm homogeneous regions like those indicated in Figure 1 are obtained. Note the presence of a peak in k (extinction coefficient) around 6.0 eV and 4.8 eV in the [O] = 0.48 and [O] = 0.19 sections of this film, respectively. This peak is present around 5-6 eV for all film compositions in the study, except for the bottom section of COQ, [O] = 1 at % .

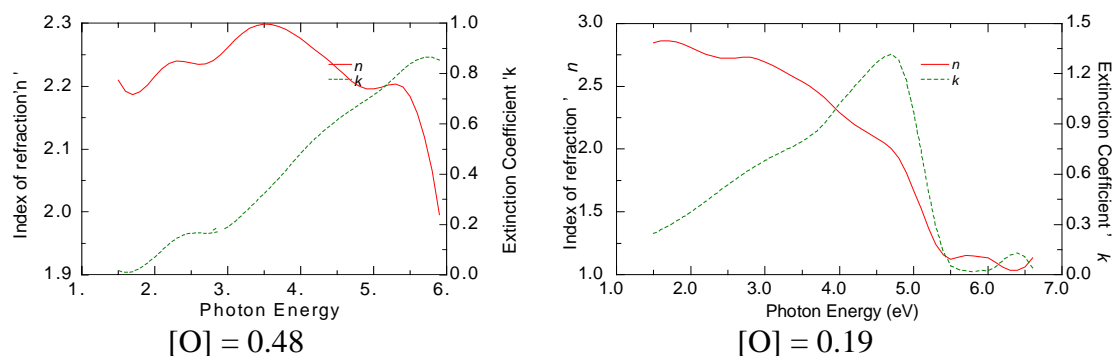


Figure 3. Spectrally resolved optical constants for both portions of the 365 nm Film. The spectra are labeled according to the oxygen content of the specimen.

Further, the peak trends toward higher energy as oxygen concentration is increased. This trend is best illustrated in Figure 4. This plot shows the correlation between this absorption peak location and oxygen concentration. Clearly, the absorption peak as measured by ellipsometry goes to higher energy with oxygen concentration, and therefore with oxygen coordination to Cr.

It seems likely that this absorption peak shift is related to the change in Cr valence as measured by XPS. At high oxygen concentrations, both XPS and composition data seem to indicate that the stoichiometry of CrOCN is much like Cr₂O₃ ($a = 1.5$). As N concentration increases to the detriment of oxygen, N may begin substituting for O in this bonding configuration. As the valence of N is probably substantially more negative than the oxygen valence of -2 , this necessitates a formal Cr valence shift to a value greater than $+3$, in the ionic limit of bonding.

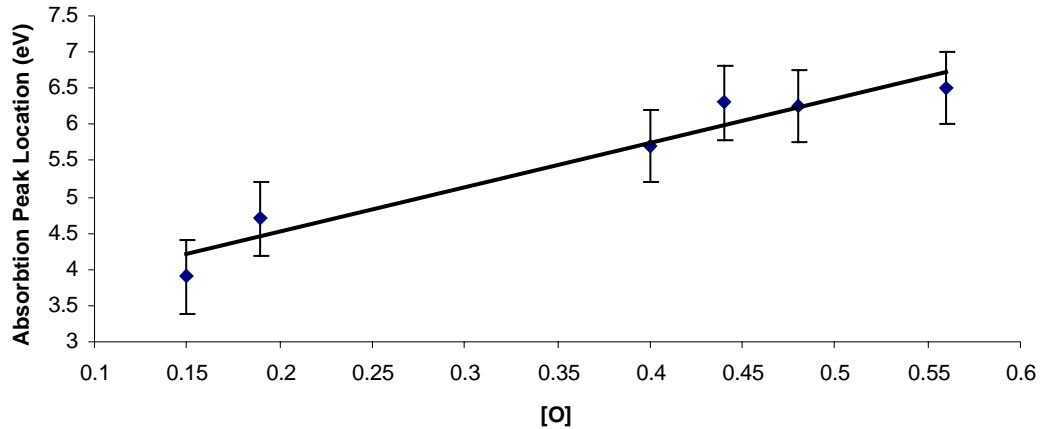


Figure 4. Absorption peak shift vs. [O]

A molecular orbital diagram representing the structures involved in this argument is shown on the left hand side of Figure 5. Cr₂O₃ is a wide band gap semiconductor ($E_g = 4.8$ eV). As N replaces O in this compound and Cr changes valence one of the t_{2g} states becomes unfilled. The right side of Figure 5 shows how this might look in terms of the molecular orbital diagram of a CrNO complex. Then, the absorption peak shift to lower energy may be consistent with the dominant optical transition changing with Cr valence. The dominant transition for Cr₂O₃ is expected to be from t_{2g} to e_g . It is possible that the dominant transition in a CrNO complex is between t_{2g} states as illustrated in the figure. As such, this transition would be expected to occur at a lower energy.

CONCLUSIONS

This study illustrates how local optical properties are dictated by atomic coordination which affects bond orbital energies, their energy dispersion and occupation. In CrOCN films used in phase shifting optical lithography, this is due to a change in Cr valence with depth as measured by XPS. This change in valence is related to the attenuation of light because of its correlation with an absorption peak seen in the optical spectra of these films. Such films provide an excellent example of how macroscopic

properties are controlled by variations in chemical and optical properties at multiple length scales.

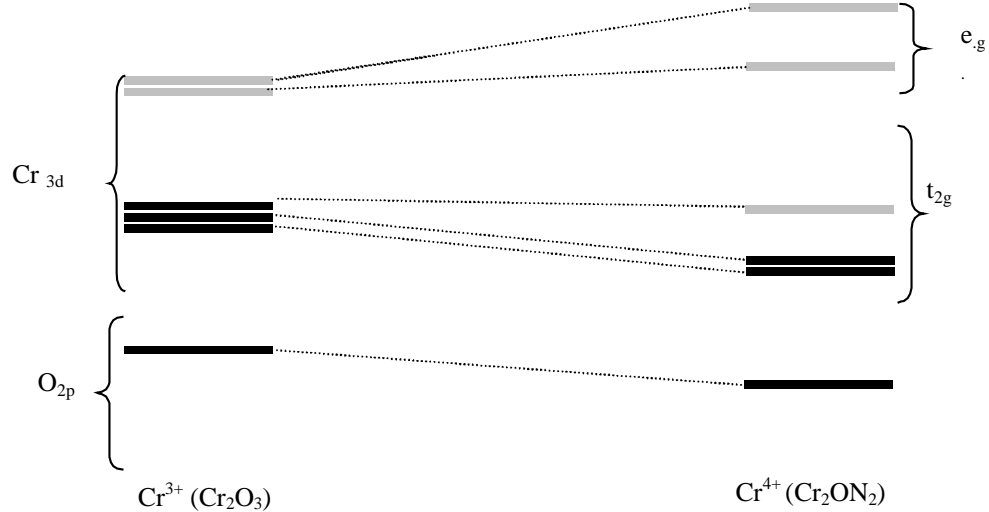


Figure 5. Molecular orbital diagrams for chromium oxide and CrON complex. Filled levels are indicated in black, unoccupied levels in gray.

REFERENCES

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