Optical properties of materials for 157 nm lithography

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by

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Microelectronic Engineering Rochester Institute of Technology

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Submitted to the
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Abstract

A survey of optical properties of sputtered materials in the spectral range of 145 nm to 800 nm has been performed. The optical constants $n$ and $k$ have been measured using ellipsometric techniques. Four combination materials have been created with the properties suitable for application in Attenuated Phase Shift Mask (APSM) manufacturing. The four combination materials have also been characterized, with the results presented.
To Rose of Sharon Daly, whose incessant nagging made completion of this work possible.
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Acronyms

CD  Critical dimension. The smallest feature present in the object to be imaged.

OPC  Optical Proximity Correction. A technique that corrects for non-ideality of the imaging system by pre-distorting the object.

OD  Optical Density is the log of the attenuation factor of an optical component.

VUV  Vacuum Ultra Violet. VUV defines the spectral region of wavelength values between 15 nm and 185 nm.

DUV  Deep Ultra Violet. Spectral region of wavelength values between 185 nm and 300 nm.

RET  Resolution Enhancement Technique. A method of overcoming the theoretical resolution limit of a conventional optical imaging system.

APSM  Attenuated Phase Shift Mask. The type of mask used in microlithography that produces enhanced aerial image contrast.

MSE  Mean Square Error. The indicator of a quality of fit.

VASE  Variable Angle Spectroscopic Ellipsometry: Thin film characterization technique that allows accurate measurement of optical constants n and k.

PVD  Physical Vapor Deposition, or sputtering. Thin film deposition technique that allows control of film composition and microstructure.

IC  Integrated Circuit. An electronic device manufactured in a sequence of unit steps at a semiconductor fabrication facility.
DOF  Depth of Focus. Range of focus positions with acceptable image fidelity.

NA  Numerical Aperture of a lens.

EMA  Effective Media Approximation. A model of light-matter interaction that allows for estimation of the composite material optical properties.

XPS  X-ray photoelectron spectroscopy. An analysis technique that allows to study the composition and electronic state of the surface region of a sample.
Symbols

\( n \) refractive index.

\( k \) extinction coefficient, or imaginary part of the complex refractive index

\( \tilde{n} \) complex refractive index: \( \tilde{n} = n + ik \)

\( \varepsilon \) complex dielectric constant: \( \varepsilon = \tilde{n}^2 \)

\( \lambda \) wavelength of light.

E electric field vector

B Magnetic field vector

D electric displacement vector

E' local electric field vector

p dipole moment vector.

P average dipole moment per unit volume vector.

N concentration, or number of atoms per unit volume.

\( \alpha \) polarizability, \( p = \alpha E' \).

\( k_1 \) resolution factor

\( k_2 \) Depth of Focus factor

\( \Psi \) ellipsometric magnitude: represents the magnitude of the ratio of complex reflection coefficients for two different polarization states.
SYMBOLS

Δ ellipsometric phase difference: phase difference between the two waves with different polarization

ρ ratio of complex reflection coefficients in an ellipsometric measurement.

r_⊥ Amplitude reflection coefficient in TE case

r_∥ Amplitude reflection coefficient in TM case

R_⊥ Intensity reflection coefficient in TE case

R_∥ Intensity reflection coefficient in TM case

ΔΦ Phase Shift

q depolarization factor in the Effective Media Approximation (EMA) model
Elements and Compounds

$\text{Al}_2\text{O}_3$ alumina
Mo Molybdenum
$\text{MoN}$ Molybdenum Nitride
$\text{MoO}$ Molybdenum Oxide
$\text{CrO}_x$ Chromium Oxide
CrN Chromium Nitride
Cr Chrome
Nb Niobium
$\text{NbN}$ Niobium Nitride
$\text{Nb}_2\text{O}_5$ Niobium Oxide
Zr Zirconium
$\text{ZrN}$ Zirconium Nitride
Ti Titanium
TiN Titanium Nitride
$\text{TiO}_2$ Titanium Oxide
Ta Tantalum
TaN Tantalum Nitride
Ta$_2$O$_5$ Tantalum Oxide
SiO$_2$ Silicon Oxide
Si$_3$N$_4$ Silicon Nitride
Chapter 1

Introduction

1.1 Evaluating Microlithography Process

The performance of optical lithography and its limitations can be best quantified considering the main figures of merit: Critical dimension (CD), and Depth of Focus (DOF).

\[
CD = k_1 \frac{\lambda}{NA} \quad (1.1) \\
DOF = \pm k_2 \frac{\lambda}{NA^2} \quad (1.2)
\]

Here, CD represents the minimum feature that can be patterned with a particular optical lithography system. As can be seen, CD is dependent on three parameters of the system, resolution factor \((k_1)\), wavelength \((\lambda)\), and Numerical Aperture (NA) [1]. The resolution factor represents the “quality” of the imaging system and is higher than 0.5 for a conventional coherent setup. This is a theoretical limitation, impossible to achieve in practice. It can be approached by lowering the lens aberrations and enhancing the contrast of both the aerial image and photoresist. The other two parameters, the actinic wavelength \(\lambda\) and the imaging tool NA are much harder to change, leading to very slow rate of change, as shown in Figure 1.1.

Lowering the theoretical limit on \(k_1\) is the most cost efficient way of improving resolution. Some of the techniques that extend the limit to 0.25 include off-axis illumination, phase shift masks[2, 3], chromeless masks, etc. This work focuses on advancement of the Attenuated Phase Shift Mask (APSM) approach.
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Figure 1.1: Progress of lithography systems' resolution. Note that deep sub-wavelength resolution has become commonplace since the mid-1990's. Data source: Numerical Technologies, Inc.
1.1.1 Attenuated Phase Shift Mask

In this approach, the typical binary absorber is replaced with a phase-shifting attenuator layer. This creates a “negative” electric field in place of no field, thus enhancing contrast of the image, see Figure 1.2 [1].

![Diagram of Conventional Binary Mask and Attenuated Phase Shift Mask](image)

**Figure 1.2:** An illustration of the working principle of APSM. Note the wider dynamic range (or higher modulation) in the image on the right, resulting in higher image contrast.

The material commonly used in the conventional binary masks is a graded composite of Cr, CrN, and CrOx. It provides an Optical Density (OD) of 3 or higher at thickness values around 1 kÅ. This material cannot be used in the APSM case due to its high absorption characteristics. The requirements for a successful APSM material are listed below:

- Phase shift of $\pi$ (typical thickness of approx. 1 kÅ)
- Thickness non-uniformity better than 0.5%.
- Transmission of between 6% and 20% (tunable)
- Etch process compatible with semiconductor fabrication requirements, capable of low defect levels
- Deposition process capable of low defect levels
- Film stability under extended laser irradiation.
CHAPTER 1. INTRODUCTION

As the transmission of the APSM layer has to be adjusted according to the layout requirements, no single-component material is acceptable. The successful APSM material has to be comprised of two or more components, whose ratio will determine the final transmission at π phase shift.

While bulk material data is readily available [4], the thin film optical properties may be significantly different. Sputtered film data is available at \( \lambda = 193 \) nm [5, 6], but there is no available data at \( \lambda = 157 \) nm. The ensure that no possible winning combination is missed, a survey of the optical properties in the Vacuum Ultra Violet (VUV) spectral region has to be undertaken. After the material optical properties are collected, the candidates for APSM films have to be identified. The composite films are then to be deposited and analysed. If all of these steps are successful, the candidate materials for APSM layer for the 157 nm node can be considered identified.

1.2 Dielectric constant modeling

The complex dielectric constant \( (\varepsilon) \) of a material is defined as [7]:

\[
D = \varepsilon E = E + 4\pi P
\]

(1.3)

Here, electric displacement vector \( (D) \) is sometimes referred to as the electric field inside the dielectric. In the case of a homogeneous isotropic medium the solution can be found exactly in two steps. First, the electrostatic problem is solved to obtain local electric field \( (E') \), and dipole moment \( (p) \). Then, these two quantities are averaged to obtain their macroscopic counterparts, electric field \( (E) \) and average dipole moment per unit volume \( (P) \).

The relationship between the local electric field and the total dielectric moment is given by the Clausius–Mossotti expression [7, 8].

\[
E' = E + \frac{4\pi}{3} P
\]

(1.4)

Considering

\[
p = \alpha E' \quad \text{or} \quad P = Np = N\alpha E'
\]

(1.5)

where \( \alpha \) is polarizability of the particle and \( N \) is the concentration, or particle count per unit volume, and combining with equation (1.3), we obtain the Lorentz-Lorenz equation

\[
\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N\alpha
\]

(1.6)
1.2.1 Lorentz Oscillator

The Lorentz Oscillator model offers the simplest picture of atom-field interactions. It is purely classical, however; this model is an elegant tool for visualizing and approximating the frequency-dependent dielectric constant.

\[ m\ddot{r} + \gamma \dot{r} + \kappa r = eE'(t) \]  

where \( e \) is the charge on the electron, \( m \) is the mass of the electron.

The equation is quite common in mathematical physics, and Lorentz was aware of this. It was thus easily solved. The only term that can not be explained classically is the damping coefficient \( \gamma \). The main sources of damping are atomic collisions, and spontaneous emission.

The specific form of equation (1.7) considered by Lorentz was the case represented by

\[ E'(t) = E'_0 e^{-i\omega t} \]  

where \( E'_0 \) is a real-valued vector. The impinging electromagnetic wave thus has frequency \( \omega \) and local amplitude \( E'_0 \).

The non-dampening solution in this case is represented by

\[ r = \frac{eE'}{m(\omega^2 - \omega'^2) - i\omega\gamma} \]
CHAPTER 1. INTRODUCTION

where

$$\omega_0 = \sqrt{\frac{\gamma}{m}}$$  \hspace{1cm} (1.10)

And thus, considering that

$$\mathbf{P} = N\mathbf{p} = Ne\mathbf{r} = N\frac{e^2E'}{m(\omega_0^2 - \omega^2) - i\omega\gamma}$$  \hspace{1cm} (1.11)

we obtain

$$N\alpha = N\frac{e^2}{m(\omega_0^2 - \omega^2) - i\omega\gamma}$$  \hspace{1cm} (1.12)

Now, comparing with equation (1.6) it follows:

$$\frac{3}{4\pi} \frac{\varepsilon - 1}{\varepsilon + 2} = N\frac{e^2}{m(\omega_0^2 - \omega^2) - i\omega\gamma}$$  \hspace{1cm} (1.13)

For a gas, $\varepsilon$ can be considered close to 1, therefore $\varepsilon + 2 \approx 3$ and the commonly known form of the Lorentz dispersion relationship can be obtained:

$$\varepsilon \approx 1 + \frac{4\pi Ne^2}{m(\omega_0^2 - \omega^2) - i\omega\gamma}$$  \hspace{1cm} (1.14)

So far it has been assumed that the system has only one resonance frequency. In general, there will be many such frequencies. In this case

$$\frac{4\pi}{3} N\alpha = \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N\varepsilon^2 \sum_k \frac{f_k}{m(\omega_k^2 - \omega^2) - i\omega\gamma_k}$$  \hspace{1cm} (1.15)

where $Nf_k$ is the number of electrons corresponding to the resonance frequency $\omega_k$.

1.2.2 Free electron plasma

The Drude free-electron plasma model can be obtained from equation (1.13) by setting the restoring force to zero ($\omega_0 = 0$). In this case, the plasma frequency $\omega_p^2 = \frac{4\pi Ne^2}{m\gamma}$ and the mean time between collisions $\tau = \frac{m}{\gamma}$ are introduced. The expression is then reduced to

$$\frac{\varepsilon - 1}{\varepsilon + 2} = -\frac{1}{3} \frac{4\pi Ne^2}{m\omega^2 + i\omega\gamma} = -\frac{1}{3} \frac{\omega_p^2}{\omega^2 + i\omega\tau}$$  \hspace{1cm} (1.16)
Or, in the case of \( \varepsilon \approx 1 \)

\[
\varepsilon = 1 - \frac{\omega_p^2}{\omega^2 + i\frac{\omega}{\tau}}
\]  

(1.17)

This model has proven to be of use in representing conductive materials, where the majority contribution to field-matter interaction is due to the free electrons. In this case, the bound electrons are considered insignificant. For real-world applications, all terms should be considered, and the Drude model becomes just one of the terms in summation equation (1.15) with \( \omega_0 = 0 \).

1.2.3 Cauchy approximation

The approximate formula developed by Baron Augustin-Louis Cauchy[9], is applicable to a wide range of materials. It can be obtained from the equation (1.15) by assuming that the dielectric constant is close to one (as is for many gases), and that no absorption is present in the material. Despite these assumptions, the formula has proven to provide accurate dispersion relationship for many dielectric materials. With slight modifications, it can be extended to cover Deep Ultra Violet (DUV) and even VUV spectral regions for certain materials. It is, therefore, of great interest for this study.

To obtain the Cauchy formula, the Lorentz dispersion relationship has to be re-written in the form (assuming \( \varepsilon = \Re(\varepsilon) = n^2 \approx 1 \) and \( \gamma_k = 0 \)):

\[
n^2 - 1 = 4\pi N\alpha = \sum_k \rho_k \frac{\lambda^2 \lambda_k^2}{\lambda^2 - \lambda_k^2},
\]  

(1.18)

where

\[
\rho_k = N \frac{e^2}{\pi mc^2} f_k
\]  

(1.19)

Using the identity

\[
\frac{\lambda}{\lambda^2 - \lambda_k^2} = 1 + \frac{\lambda_k^2}{\lambda^2 - \lambda_k^2},
\]  

(1.20)

and applying the Taylor expansion series

\[
n^2 - 1 = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \cdots \\
- B'\lambda^2 - C'\lambda^4 - \cdots
\]  

(1.21)
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where

\[ A = \sum_k \rho_k \lambda_k^2, \quad B = \sum_k \frac{\rho_k \lambda_k^4}{c^2}, \quad C = \sum_k \frac{\rho_k \lambda_k^6}{c^4}, \quad \ldots \]

\[ B' = \sum_k \rho_k c^2, \quad C' = \sum_k \frac{\rho_k}{\lambda_k^2}, \quad \ldots \]  

(1.22)

In the absorption-free region, where the value of refractive index \(n\) differs little from unity, \(n^2 - 1\) may be replaced by \(2(n - 1)\). Moreover, the terms \(B', C', \ldots\) usually do not exhibit appreciable influence. Therefore, if only terms no smaller than \(O\left(\frac{1}{\lambda^2}\right)\) are retained, the equation (1.21) can be reduced to Cauchy’s formula:

\[ n = 1 + A_1 \left(1 + \frac{B_1}{\lambda^2}\right) \]  

(1.23)

where

\[ A_1 = \frac{A}{2}, \quad B_1 = \frac{Bc^2}{A} \]  

(1.24)

1.3 Effective Medium Models

1.3.1 Wiener Bounds

Let us consider the bounds on the dielectric constant of a heterogeneous material, consisting of two (or more) homogeneous components[10, 11, 12].

Boundary perpendicular to field

In the simplified case of periodic assembly of layers of two disparate materials, components 1 and 2. Let \(t_1\), and \(t_2\) be the thickness of each layer; while \(\varepsilon_1\), and \(\varepsilon_2\) are the corresponding dielectric constant of each component.

Consider a plane monochromatic wave incident on the structure in Figure 1.4 with the electric field vector perpendicular to the planes. If the characteristic dimensions of the structure \((t_1, t_2)\) are small compared to the wavelength of light \(\lambda\), the field inside the layers can be considered uniform. The normal component of the electric displacement vector \(D\) must be continuous at the materials boundaries. Therefore

\[ E_1 = \frac{D}{\varepsilon_1}, \quad E_2 = \frac{D}{\varepsilon_2}, \]  

(1.25)
Figure 1.4: A periodic assembly of disparate layers.
and the mean electric field averaged over volume is

$$\mathbf{E} = \frac{t_1 \mathbf{D}_{1} + t_2 \mathbf{D}_{2}}{t_1 + t_2}$$  \hspace{1cm} (1.26)$$

The effective dielectric constant of media in this case is

$$\varepsilon_{\perp} = \frac{\mathbf{D}}{\mathbf{E}} = \frac{t_1 + t_2}{t_1 \varepsilon_1 + t_2 \varepsilon_2}$$  \hspace{1cm} (1.27)$$

or

$$\varepsilon_{\perp}^{-1} = f_1 \varepsilon_1^{-1} + f_2 \varepsilon_2^{-1}$$  \hspace{1cm} (1.28)$$

where

$$f_1 = \frac{t_1}{t_1 + t_2}, \text{ and } f_2 = \frac{t_2}{t_1 + t_2} = 1 - f_1$$  \hspace{1cm} (1.29)$$

This case is represented by the curved line in Figure 1.5.

**Boundary Parallel to field**

In the case with the electric field vector parallel to the layer boundaries in Figure 1.4 on the preceding page the electric field itself is continuous at the boundary. Thus

$$\mathbf{D}_1 = \mathbf{E} \varepsilon_1, \quad \mathbf{D}_2 = \mathbf{E} \varepsilon_2$$  \hspace{1cm} (1.30)$$

and the mean value of $\mathbf{D}$ is

$$\mathbf{D} = \frac{t_1 \mathbf{E} \varepsilon_1 + t_2 \mathbf{E} \varepsilon_2}{t_1 + t_2}$$  \hspace{1cm} (1.31)$$

with the effective media dielectric constant

$$\varepsilon_{\parallel} = \frac{\mathbf{D}}{\mathbf{E}} = \frac{t_1 \varepsilon_1 + t_2 \varepsilon_2}{t_1 + t_2} = f_1 \varepsilon_1 + f_2 \varepsilon_2$$  \hspace{1cm} (1.32)$$

This case is represented by the straight line in Figure 1.5.
Figure 1.5: An example of the Wiener bounds for two materials. The two materials are represented by the dots labeled $\varepsilon_1$ and $\varepsilon_2$. The two lines represent the possible mixed materials for the two limiting cases. The area $\Omega(\varepsilon_1, \varepsilon_2)$ bound by $\varepsilon_\parallel$ and $\varepsilon_\perp$ represents all of the possible materials that can be obtained by mixing $\varepsilon_1$ and $\varepsilon_2$. 
Intermediate cases

While the values $\varepsilon_\parallel$, and $\varepsilon_\perp$ above represent a small portion of real-life scenarios, they were found to bind the effective dielectric constant of an arbitrary mixture of the two materials. In other words, for any possible physical structural form of mixing the two materials with dielectric constants $\varepsilon_1$ and $\varepsilon_2$, the resulting dielectric constant $\varepsilon_{eff}$ has to lie within the region $\Omega(\varepsilon_1, \varepsilon_2)$ defined by the expressions $\varepsilon_\parallel$, and $\varepsilon_\perp$ ((1.32) and (1.28), respectively). Any combination of the two materials, with any fractional weighting $f_1$, with any structure of the composite material, has to have its dielectric constant $\varepsilon_{eff}$ in the region defined by the Wiener bounds. A more strict restriction, considering some microstructure information is explored below.

1.3.2 Effective Media Approaches

Let us consider a case of two (or more) materials intermixed on a molecular scale. Applying the Lorentz-Lorenz equation (1.6) on page 4 independently to both materials we obtain

$$\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} = \frac{4\pi}{3} N_1 \alpha_1, \quad \frac{\varepsilon_2 - 1}{\varepsilon_2 + 2} = \frac{4\pi}{3} N_2 \alpha_2$$

(1.33)

Combining the above with equation (1.6) and

$$N\alpha = N_1 \alpha_1 + N_2 \alpha_2$$

(1.34)

we obtain

$$\frac{\varepsilon - 1}{\varepsilon + 2} = f_1 \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} + f_2 \frac{\varepsilon_2 - 1}{\varepsilon_2 + 2}$$

(1.35)

where

$$f_{1,2} = \frac{N_{1,2}}{N_1 + N_2}$$

(1.36)

is the volume material fraction.

The expression (1.35) is the basis of all EMA models, which differ in defining $\varepsilon$ with relation to the constituent values $\varepsilon_1$, and $\varepsilon_2$. 
Bruggeman model

In the Bruggeman Model [13] the self-consistent assumption is made. The dielectric constant of the medium in which the particles are suspended is taken to be the same as the complex dielectric constant (ε) of the composite medium. With that assumption, we obtain:

\[
\frac{f_1}{\varepsilon_1 + K\varepsilon} + \frac{f_2}{\varepsilon_2 + K\varepsilon} + \frac{f_3}{\varepsilon_3 + K\varepsilon} + \cdots = 0
\]

(1.37)

Here, multiple types of particles are embedded in the same medium. The value of \( K = 2 \) represents the assumption of spherical microstructure (this assumption was used to obtain equation (1.6)). In principle, the Bruggeman theory should be valid for all values of \( f \) as it treats the components in the mixture on an equal basis. However, when one component’s ratio is much higher than the other’s, the retarding nature of the induced polarization must be taken into account.

Maxwell Garnett Model

This approach makes the assumption that one or more materials (\( \varepsilon_2 \), or \( \varepsilon_3 \)) are suspended in the host medium of another material (\( \varepsilon_1 \)) [14].

\[
\frac{\varepsilon_1 -\varepsilon}{\varepsilon + 2\varepsilon_1} = f_2 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} + f_3 \frac{\varepsilon_3 - \varepsilon_1}{\varepsilon_3 + 2\varepsilon_1}
\]

(1.38)

where \( f_1, f_2, \) and \( f_3 \) are fractional weights of the constituents, with \( f_1 + f_2 + f_3 = 1 \). As is implied in its derivation, this formula is asymmetrical with respect to the choice of the host. The accuracy of this approach is best when one material is present in overwhelming amount. Therefore, this approach is limited to small volume fractions \( f_2 \) and \( f_3 \).

The Effective Media Approximation model

The combination of both approaches, the EMA theory developed by Aspnes[8] can explain both Maxwell Garnett and Bruggeman cases. The effective dielectric function in the EMA theory is defined as

\[
\varepsilon = \frac{\varepsilon_1\varepsilon_2 + \bar{\varepsilon}(f_1\varepsilon_1 + f_2\varepsilon_2)}{\bar{\varepsilon} + (f_1\varepsilon_2 + f_2\varepsilon_1)}
\]

(1.39)

where

\[
\bar{\varepsilon} = \frac{(1 - q)\varepsilon_{\text{host}}}{q}
\]

(1.40)
Here, $q$ is a screening parameter (or the depolarization factor) with the range 0–1. The actual value of the depolarization factor ($q$) is determined by the specific geometrical configuration of the particles. Namely, the Wiener bounds are given by $q = 0$, and $q = 1$, while the two-dimensional macroscopically isotropic case is represented by $q = 1/2$, and the three-dimensional case of perfect mixing is given by $q = 1/3$. An example of the change in optical properties with varying $q$ is given in Figure 1.6.

**Figure 1.6**: An example of the variation in optical properties according to the EMA model. The $\epsilon_{\text{EMA}}$ line represents $q$ varying from 0 to 1, while $f_1 = 0.7$.

### 1.4 Fresnel equations

The Fresnel equations[15] give the ratio of the reflected electric field amplitude to the incident electric field for electromagnetic radiation incident on a material boundary. These equations are integral to modeling of the material properties...
based on ellipsometric measurements. The reflectance coefficients for both polarization states can be modeled using the material data, thin film model of the physical structure and the Fresnel equations. The material data (n and extinction coefficient (k)) can be thus determined if the physical structure used in the model is correct.

\[ r_\perp = \left| \frac{\tilde{E}_r}{\tilde{E}_i} \right| = \frac{n_1 \cos \theta - n_2 \cos \theta_i}{n_1 \cos \theta + n_2 \cos \theta_i} \quad (1.41) \\
\]

Using Snell’s law

\[ \tilde{n}_1 \sin \theta = \tilde{n}_2 \sin \theta_t \quad (1.43) \]

the equations can be simplified to:

\[ r_\perp = -\frac{\sin(\theta - \theta_t)}{\sin(\theta + \theta_t)} \quad (1.44) \]
\[ r_\parallel = \frac{\tan(\theta - \theta_t)}{\tan(\theta + \theta_t)} = \frac{\sin \theta_t \cos \theta - \sin \theta \cos \theta_t}{\sin \theta \cos \theta + \sin \theta_t \cos \theta_t} \quad (1.45) \]
In the case of normal incidence, the magnitudes of $r_\perp$ and $r_\parallel$ are equal, and are reduced to

$$-r_\perp = r_\parallel = \frac{\tilde{n}_2 - \tilde{n}_1}{\tilde{n}_2 + \tilde{n}_1} \quad (1.46)$$

$$R_\perp = R_\parallel = \left| \frac{\tilde{n}_2 - \tilde{n}_1}{\tilde{n}_2 + \tilde{n}_1} \right|^2 \quad (1.47)$$

### 1.5 Phase Shift and Transmission

Direct measurement of phase shift at 157 nm is not currently possible, therefore, the measured $n$ and $k$ values were used to model the phase shift and the transmission of the proposed APSM materials.

The transmission loss due to absorption in the phase shift film is

$$T_{abs} = e^{-\frac{4\pi}{\lambda} kd} \quad (1.48)$$

where $d$ is the physical thickness of the film. Considering the relative transmission with respect to the clear areas on the mask,

$$T_{rel} = \frac{(1 - R_{12})(1 - R_{23})}{1 - R_{13}} \cdot e^{-\frac{4\pi}{\lambda} kd} \quad (1.49)$$

Here, the reflectance coefficients are calculated using Fresnel equations (1.47)

$$R_{12} = \left| \frac{\tilde{n}_1 - \tilde{n}_2}{\tilde{n}_1 + \tilde{n}_2} \right|^2 = \frac{(n_1 - n_2)^2 + (k_1 - k_2)^2}{(n_1 + n_2)^2 + (k_1 + k_2)^2} \quad (1.50)$$
The phase shift is calculated similarly, with the phase shift in the APSM film when compared to the phase shift in air given by

\[
\Delta \Phi = \frac{2\pi}{\lambda} (n_2 - n_3) d + \Delta \Phi_{12} + \Delta \Phi_{23} - \Delta \Phi_{13}
\]

(1.51)

The interfacial phase term is given by

\[
\Delta \Phi_{12} = \text{arg} \left( \frac{\tilde{n}_1}{\tilde{n}_2} \right)
\]

(1.52)

### 1.6 Modeling of Composite APSM materials

In addition to EMA modeling described in Section 1.3 some more detailed analysis had to be performed before the composite materials could be deposited. Utilizing the models in Section 1.3, the atomic fraction of the absorber material can be determined. The fractional volume occupied by each material can be calculated using

\[
v = f \frac{A}{\rho}
\]

(1.53)

where \(v\) is the volume fraction, \(f\) is the atomic fraction, \(A\) is the atomic weight, and \(\rho\) is the density of the material in consideration. The volume fraction can thus be calculated by normalizing the total volume:

\[
v_1 + v_2 = 1 \quad \Rightarrow \quad v_1 = \frac{v_{1,rel}}{v_{1,rel} + v_{2,rel}}
\]

(1.54)

\[
v_1 = \frac{1}{1 + \frac{f_2 A_2 \rho_2}{f_1 A_1 \rho_1}}
\]

(1.55)

After the thickness ratios of the two materials have been calculated, deposition tool power ratios need to be modeled. This is done using the procedure described in Section 2.1.5. The total deposition time is adjusted using equation (2.1) to achieve \(\pi\) phase shift. The procedure for modeling the phase shift based on predicted optical constants \(n\) and \(k\) is described in Section 1.5.
Chapter 2

Experimental

2.1 Thin film deposition

Optical requirements for the materials under study dictate the thickness of the materials in question. These considerations, along with manufacturing compatibility, lead to Physical Vapor Deposition (PVD) as the process technique. This technique allows to deposit very thin films with highly controlled and customizible physical properties. The setup of the sputter (PVD) chamber at RIT allowed for a physical mixture of two materials to be deposited. Two distinct methods of intermixing the materials are possible

- Atomic level mixing, or deposition of layers of average thickness on the order of 1 Å or less
- Superlattice type structure, or deposition of discrete layers with thickness on the order of 1/10 of the wavelength of interest

For this research, the two-target approach, or the atomic level mixing was utilized.

2.1.1 Capacitatively Coupled Glow discharge plasma

The plasma used in sputtering is typically characterized as “nonthermal” plasma [16, 17, 18]. This describes the condition of matter in which the electrons are very energetic while the bulk of the molecules are near ambient temperature. To create this condition, the ionized matter has to be present in gas form, at the pressure between 1 mTorr and 50 mTorr. A negative electrode is introduced into the
vicinity of the gas, accelerating the existing gas ions towards it. These ions bomb-
bard the cathode, discharging secondary electrons, which are rapidly accelerated
away from the cathode. These high energy electrons ionize the gas molecules on
impact, the ions bombard the cathode and the process is thus sustained. The
ionization process produces a photon, which is responsible for the “Glow” part
of the process description.

2.1.2 Sputtering

To utilize this process to produce thin films, a target made of the material to
be sputtered is placed on the cathode. Argon is used as the plasma gas. The
advantageous properties of Ar gas are that it is inert, and readily available in
Ultra High Purity form. The atomic weight of Ar allows the ions to accelerate
to high enough velocity to dislodge globules of material from the target. The
globules ejected from the target land on the substrate located in the vicinity, and
form a film. Typical deposition rates can vary from as low as 0.5 Å/s to a few
1000 Å/s, depending on the power density applied to the target and the target
to substrate distance.

![Figure 2.1: A typical sputtering chamber setup.](image-url)
The limitations of the sputtering process are

- The lowest process pressure is approximately 1 mTorr. If the pressure is lowered below this value, the mean free path of the electrons ejected from the cathode becomes larger than the dimensions of the chamber and the ionization rate is not high enough to sustain the plasma. This means that the deposition takes place in low-grade vacuum, instead of high, or ultra-high vacuum. The potential for contamination is greater compared to ultra-high vacuum techniques.

- The substrate is exposed to plasma. This can have far-reaching negative effects in terms of plasma damage, charge accumulation, etc. However, because no charge sensitive devices are being made this case, the effects of surface plasma treatment on the films in question is negligible.

### 2.1.3 Reactive sputtering using RF power source

If the sputtering gas contains any reactive species (such as oxygen or nitrogen) the material composition of the film may differ from the composition of the target. These reactive species can combine with the target material to produce oxides and nitrides of the original material. The reaction typically takes place at locations with high energy availability. Those locations include the target and the substrate. Depending on the relationship between the sputtering rate and the reaction rate, the oxide layer can form in both locations. If the reaction takes place on the substrate, it is possible to obtain under-stoichiometric films, if the source material arrival rate exceeds the reaction rate. If the reaction occurs mostly at the target, a different problem presents itself. The oxides and nitrides of various materials are typically electrical insulators, preventing the charge from reaching the surface of the target. In this case, as ions bombard the target, it accumulates positive charge until the electric field is high enough to prevent any more ions from reaching the target.

In such a case (or if the target itself is made of an insulating material), the cathode is attached to an RF power supply. Unlike with DC-mode power supply, the RF power supply provides both positive and negative voltages. During the negative part of the duty cycle, the ions are attracted to the target and sputtering commences. During the positive part of the duty cycle, the electrons are attracted to the target (with much greater mobility) and neutralize the ions collected at the surface. More electrons arrive than ions, and the target carries an average
negative charge at the surface, resulting in DC-bias. This value can be measured and is typically used to analyze the state of plasma in PVD chambers.

2.1.4 Single target mode vs. Dual target mode

Deposition of composite films can be carried out in two distinct fashions with the RIT PE2400 chamber target setup (see Figure 2.2).

![Diagram of dual target chamber setup](image)

Figure 2.2: Dual target chamber setup, with both targets on at the same time.
One target is turned on at a time

- Discreet films of each material are deposited.
- Mostly laminar-type structure, with boundaries parallel to the electric field
- Maximum film thickness of \( \approx \lambda/10 \) is used
- Total of 4 film pairs, with between 12 and 60 table revolutions per film

Both targets are on at the same time

- Materials are mixed on the atomic scale
- less than 2 Å of material is deposited per pass under each target
- Approx. 350 table revolutions are required to produce an APSM film

2.1.5 Deposition of Composite Materials

After the theoretical modeling had been performed, the desired film optical parameters are known. In the process of modeling, the desired film thickness and ratio of constituents are generated. The required power ratio was calculated using the equation (2.1).

\[
d_{\text{comp}} = (r_1 \cdot P_1 + r_2 \cdot P_2) t
\]

Here \( d_{\text{comp}} \) is the composite film thickness in Å, \( r_1 \) and \( r_2 \) are the deposition rates of the two materials \( \left( \text{in } \frac{\text{Å}}{\text{min} \cdot \text{W}} \right) \), and \( t \) is the deposition time. Considering that the total deposition power was determined by tool capabilities: \( P_{\text{total}} = P_1 + P_2 \), the equation (2.1) can be solved for the respective power levels \( P_1 \) and \( P_2 \). These power levels then had to be set for the two targets and delivered simultaneously.

In a PVD process the power cannot be measured directly at each target, only at the power supply. In order to estimate the power delivered to each of the two targets the bias voltage was used as an indicator. In a single target chamber the power and bias voltage have a definitive relationship, \( i.e. \) a certain voltage level corresponds to only one power level and vice versa (see Figure 2.3). While this may not be perfectly accurate in the case of a multiple target chamber, the approach of relating power to bias voltage deviates minutely from the truth. In order to establish the relationship between the delivered power and the induced bias voltage a separate experiment was performed for each of the targets with the
Figure 2.3: The data used for power calibration in the composite mode of sputtering. Note the different power range for Si and Nb targets. This corresponds to the different amount of the materials desired in the composite
corresponding process conditions. In this experiment, a certain known amount of power is delivered to a single target, and the bias voltage is recorded. With this data collected for both targets, it is then possible to deduce the amount of power delivered to each of the multiple targets in the co-deposition process.

During the process development for the composite films, several dry runs were performed in order to arrive at the correct power split value. The power splitter and the total power level were adjusted until the desired voltage was achieved on each of the two targets used for deposition. The power splitter setting and the power level were recorded and used in the subsequent iteration of the process, if necessary.

### 2.2 Thin film characterization

#### 2.2.1 Profilometry

The simplest method of determining the thickness of a thin film is via profilometry. In this technique, a stylus scans across the sample, following the surface profile. Deviations in the vertical position of the stylus are measured and reported to the user. If the scanned sample contains a step, the step's height can be measured (see Figure 2.4 on the following page).

The profilometer's resolution in the vertical (or height) dimension is limited by the sensing electronics and vibration isolation of the setup. It is typically on the order of a few Angstrom or less. The most challenging part of using the profilometry technique for film thickness measurements proved to be generating of the consistent step in the film.

#### 2.2.2 Spectrophotometry

One of the most basic optical properties of a thin film critical to this study is its transmittance. The transmission of an object can be measured directly using a spectrophotometer. In a spectrophotometer setup, the intensity of a beam that has passed through an object is compared to the intensity of a beam passing through empty space, and the ratio of the two values is taken to be the transmission of the film. For this work, two measurement apparatus' were used: a Perkin-Elmer Lambda UV11 spectrophotometer with available range of 190 nm to 900 nm, and the VASE tool in transmission measurement mode. Both tools were used with the beam normal to the surface of the film, which was deposited onto either a quartz, or a CaF₂ substrate.
Figure 2.4: A schematic representation of a profilometer scan.

Figure 2.5: Example of a spectrophotometric measurement.
2.2.3 Ellipsometry

The ellipsometry approach does not rely on measurements of intensity of reflected or transmitted light, but rather on its polarization state [19]. The two parameters measured during an ellipsometric run are $\Psi$ and $\Delta$, defined as

$$
\rho = \frac{r_\perp}{r_\parallel} = \tan \Psi e^{i\Delta}
$$

(2.2)

where $\rho$ represents the ratio of complex reflection coefficients for the two different polarization states $s$ and $p$ (see Section 1.4 on page 14).

These parameters are measured at multiple incidence angles (typically 3) and over a large spectral region (typically 140 nm to 800 nm). Thus, a set of 6 vector measurements is obtained (3 angles × 2 parameters across wide spectral range). These parameters are then modeled using the assumed knowledge of films optical constants and film thickness. Typically, only one set of optical constants is unknown (the film in question), and one or two thickness values for the film stack are unknown. Thus, by using the equations in section 1.4 the 2 unknown vector quantities ($n$ and $k$) are fitted to the 6 measured vector parameters ($\Psi$ and $\Delta$ × 3 angles). The Mean Square Error (MSE) is used as the quality of fit indicator.

$$
\text{MSE} = \frac{1}{N} \sum_{i=1}^{N} \left( \left| \frac{\Delta_i^{\text{exper}} - \Delta_i^{\text{model}}}{\sigma_i^{\Delta}} \right|^2 + \left| \frac{\Psi_i^{\text{exper}} - \Psi_i^{\text{model}}}{\sigma_i^{\Psi}} \right|^2 \right)
$$

(2.3)

where $\Psi$ and $\Delta$ represent the measured and modeled ellipsometric parameters (see equation (2.2)), and $\sigma^{\Delta}$ and $\sigma^{\Psi}$ are the standard deviations of the measured values.

The values of $n$ and $k$ are modeled using the common material models described in Section 1.2 on page 4.
Chapter 3

Results

The results of this work are twofold: a database of material optical properties in the VUV spectral region, as well as a demonstration of composite film with properties suitable for APSM use.

3.1 Materials Database

Table 3.1 includes all of the materials that were measured in the survey portion of this thesis. Both $n$, $k$, and $\varepsilon$ (where $\varepsilon = (n + ik)^2$) are given. Standard deposition conditions were used. In the cases when acceptable film quality was not achieved, the process was optimized. The film thickness was measured using a step created with photoresist on a separate sample. A physical profilometer technique was used to measure the thickness. This deposition rate was used to estimate of the material fraction ratio in the subsequent co-deposition experiments.

For each one of the materials in Table 3.1 a set of ellipsometric measurements was obtained. These data, ellipsometric magnitude ($\Psi$) and ellipsometric phase difference ($\Delta$) were then fitted to a thin film stack model with variable $n$, $k$, and film thickness using the Fresnel equations (1.42). An example of the model fit can be seen in Figures 3.1 and 3.2. The results of the fit were taken to be the measured optical constants (see Figure 3.3). Fitted thickness was compared to the thickness measured with a profilometer as a consistency check.

A summary of the optical properties at $\lambda = 157$ nm is shown in Figure 3.5. The two lines represent all of the possible materials that would have a certain
Table 3.1: A list of materials surveyed, material constants are measured at $\lambda = 157$ nm. Materials deposited using reactive sputtering are marked with "-r", while non-reactively deposited films are marked with "-n".

<table>
<thead>
<tr>
<th>Material</th>
<th>$n$</th>
<th>$k$</th>
<th>$\Re(\varepsilon)$</th>
<th>$\Im(\varepsilon)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$-r</td>
<td>2.091</td>
<td>0.106</td>
<td>4.361</td>
<td>0.443</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$-n</td>
<td>2.053</td>
<td>0.207</td>
<td>4.172</td>
<td>0.850</td>
</tr>
<tr>
<td>$\text{CrO}_x$</td>
<td>1.431</td>
<td>0.832</td>
<td>1.356</td>
<td>2.381</td>
</tr>
<tr>
<td>$\text{CrN}$</td>
<td>1.120</td>
<td>0.781</td>
<td>0.644</td>
<td>1.749</td>
</tr>
<tr>
<td>Nb</td>
<td>0.918</td>
<td>0.758</td>
<td>0.268</td>
<td>1.392</td>
</tr>
<tr>
<td>NbN</td>
<td>1.706</td>
<td>1.022</td>
<td>1.866</td>
<td>3.487</td>
</tr>
<tr>
<td>$\text{Nb}_2\text{O}_5$</td>
<td>1.808</td>
<td>1.035</td>
<td>2.198</td>
<td>3.743</td>
</tr>
<tr>
<td>Ta</td>
<td>1.113</td>
<td>1.371</td>
<td>-0.641</td>
<td>3.052</td>
</tr>
<tr>
<td>TaN</td>
<td>1.538</td>
<td>0.983</td>
<td>1.399</td>
<td>3.024</td>
</tr>
<tr>
<td>$\text{Ta}_2\text{O}_5$</td>
<td>1.569</td>
<td>1.516</td>
<td>0.164</td>
<td>4.757</td>
</tr>
<tr>
<td>Mo</td>
<td>0.719</td>
<td>1.492</td>
<td>-1.709</td>
<td>2.145</td>
</tr>
<tr>
<td>MoN</td>
<td>1.212</td>
<td>1.516</td>
<td>-0.819</td>
<td>3.675</td>
</tr>
<tr>
<td>MoO</td>
<td>1.164</td>
<td>1.367</td>
<td>-0.514</td>
<td>3.182</td>
</tr>
<tr>
<td>Zr</td>
<td>1.440</td>
<td>0.818</td>
<td>1.404</td>
<td>2.356</td>
</tr>
<tr>
<td>ZrN</td>
<td>1.844</td>
<td>1.512</td>
<td>1.114</td>
<td>5.576</td>
</tr>
<tr>
<td>Ti</td>
<td>1.057</td>
<td>1.081</td>
<td>-0.051</td>
<td>2.285</td>
</tr>
<tr>
<td>TiN</td>
<td>1.472</td>
<td>1.458</td>
<td>0.041</td>
<td>4.292</td>
</tr>
<tr>
<td>$\text{TiO}_2$</td>
<td>1.537</td>
<td>1.270</td>
<td>0.749</td>
<td>3.904</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>1.676</td>
<td>0.049</td>
<td>2.807</td>
<td>0.164</td>
</tr>
<tr>
<td>$\text{Si}_3\text{N}_4$</td>
<td>1.782</td>
<td>0.890</td>
<td>2.383</td>
<td>3.172</td>
</tr>
</tbody>
</table>
Figure 3.1: An example plot of the experimental and modeled $\Psi$ values for CrO$_x$. The final fitted thickness was 1071 Å.

Figure 3.2: An example plot of the experimental and modeled $\Delta$ values for CrO$_x$. 
CHAPTER 3. RESULTS

Figure 3.3: An example plot of the optical properties of CrO$_x$ obtained after fitting of the data.

Figure 3.4: The dielectric constant of CrO$_x$. 
transmission at $\pi$ phase shift. These lines can be described by combining equations (1.49) and (1.51)

$$
k' = \frac{\ln \frac{(1-R_{12})(1-R_{23})}{(1-R_{13})T}}{2(\pi - \Delta \Phi_{12} - \Delta \Phi_{23} + \Delta \Phi_{13})} (n - 1) \tag{3.1}
$$

where $T$ is the desired transmission, and the material notation is given in Figure 1.8 on page 16.

As is evident from Figure 3.5, no material’s optical properties fall in the desired transmission region defined by the two lines. Therefore, there are no single-component materials suitable for use as an APSM layer. However, there are multiple materials that fall in the bottom-right part of the figure ($k$ is too low, material too transparent) and in the top-left part ($k$ is too high, material too dark) It was the goal of the second part of this thesis to engineer a composite material using two presented in Figure 3.5, one that is too transparent (host) and one that is too dark (absorber).
3.2 Composite Materials

Study of the composite materials consisted of four major steps:

- modeling the composite (See Section 1.6)
- actual deposition (See Section 2.1.5)
- measurement of transmission and phase shift (See Sections 2.2.2, 2.2.3, and 1.5)
- reiterate

3.2.1 Analysis

The film measurement process was the same as in the case of single material films. The ellipsometric parameters $\Psi$, and $\Delta$ were measured. The optical constants $n$, and $k$ were obtained via model fitting as described in Section 2.2.3 on page 26. This set of optical constants was then referred to as the measured optical constants. This was done to differentiate them from another set of $n$ and $k$ that were obtained using the single material data and EMA modeling (see Section 1.3), which are referred to as the modeled $n$ and $k$. The comparison of the two sets of optical parameters lead to fine-tuning of the EMA model and its parameters.

The resulting composite films were thus treated as an optically homogeneous film. The maximum feature size was on the order of 5Å thick, which is much less than $\lambda/10$ therefore this assumption is valid.

After the ellipsometric analysis was carried out on all of the films, and the measured optical constants $n$ and $k$ were determined, they were used to calculate the phase shift of the material deposited at 157nm. The thickness $d_\pi$ was then re-calculated to adjust for $\pi$ phase shift. The transmission $T_\pi$ was then modeled at the thickness $d_\pi$. If the transmission $T_\pi$ deviated too much from the expected value, the model was adjusted and the deposition repeated.

3.3 Summary of Measured Films’ Properties at 157 nm

Four materials have been deposited in mixed mode with SiO$_2$ as host in all cases. The list of materials, along with the measured physical properties at $\lambda = 157$ nm is given in Table 3.2.
CHAPTER 3. RESULTS

Figure 3.6: Transmission for the final APSM candidate materials.

Table 3.2: List of composite materials deposited. The transmission is given at 157 nm and the thickness is adjusted for \( \pi \) phase shift.

<table>
<thead>
<tr>
<th>Host</th>
<th>Material</th>
<th>( T_\pi ) (%)</th>
<th>q</th>
<th>n</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>CrO(_x)</td>
<td>10.4</td>
<td>0.93</td>
<td>1.677</td>
<td>0.230</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>MoO</td>
<td>8.3</td>
<td>0.80</td>
<td>1.761</td>
<td>0.284</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>Nb(_2)O(_5)</td>
<td>10.0</td>
<td>1.00</td>
<td>1.687</td>
<td>0.236</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>Ta(_2)O(_5)</td>
<td>11.0</td>
<td>0.86</td>
<td>1.872</td>
<td>0.281</td>
</tr>
</tbody>
</table>
CHAPTER 3. RESULTS

The fraction of the material cannot be controlled explicitly during the deposition process, however, it can be estimated from the optical constants' measurements. The ellipsometric modeling (as described in Section 2.2.3 on page 26) is carried out with the EMA model instead of a single-film model. For this approach to be successful, accurate knowledge of the optical constants of both of the constituent materials is required. These constants are obtained from the survey portion of this work. As a result of such modeling it is possible to obtain the estimated volume fraction of the minority material, as well as the value of the depolarization factor $q$. The value of $q$ can provide insight into the physical structure of the material, as discussed in Section 1.3.2 on page 13.

The material composition has also been measured experimentally on most of the final APSM candidate films. The data obtained via the X-ray photoelectron spectroscopy (XPS) technique is given in Appendix A. The XPS data represents the ratio of the respective metal to Si only.

3.4 Conclusions

A database of materials applicable for APSM manufacturing at 157 nm has been compiled and characterized. The material data has been made available via the web [6].

Models have been developed for analysis of composite materials. These models (utilising our VUV data) have also been made available. Using the models, four candidate composite materials have been selected. APSM materials have been produced and shown to have their optical properties suitable for mask manufacturing.
References


REFERENCES


Appendix A

XPS data on selected APSM candidates

Selected composition data of the final APSM films listed in Table A.1. The elemental analysis of the selected films was carried out via XPS. As can be seen, there is a slight difference in the composition between the surface and 14.5 nm deep scans (depth achieved by sputtering away the material). This may be caused by the preferential sputtering of metal atoms. The presence of Carbon at the surface is likely due to contamination during handling. Another important aspect of the scans is absence of noticeable levels of Nitrogen bonds, signifying low contamination levels from air leaks in the vacuum system.

Table A.1: Summary of material fractions in manufactured APSM films as measured by XPS. The ratio of respective metal to Si is given.

<table>
<thead>
<tr>
<th>Host</th>
<th>Material</th>
<th>$f_{metal}$ (surface)</th>
<th>$f_{metal}$ (145Å depth)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>CrO$_x$</td>
<td>0.17</td>
<td>0.23</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>MoO</td>
<td>0.16</td>
<td>0.15</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Nb$_2$O$_5$</td>
<td>0.21</td>
<td>0.29</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Ta$_2$O$_5$</td>
<td>–</td>
<td>0.28</td>
</tr>
</tbody>
</table>
Figure A.1: XPS spectrum of Nb-based APSM film, taken at the surface
Figure A.2: XPS spectrum of Nb-based APSM film, taken at 14 nm under the surface.
Figure A.3: XPS spectrum of Mo-based APSM film, taken at the surface.
APPENDIX A. XPS DATA ON SELECTED APSM CANDIDATES

Figure A.4: XPS spectrum of Mo-based APSM film, taken at 14 nm under the surface.
Figure A.5: XPS spectrum of Cr-based APSM film, taken at the surface.
Figure A.6: XPS spectrum of Cr-based APSM film, taken at 14 nm under the surface.