Anisotropy of glancing angle deposited films: results of atomistic simulation

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Abstract. Anisotropy of SiO2 films fabricated by glancing angle deposition is investigated using the classical atomistic simulation and anisotropic Bruggeman effective medium theory. The voids between the slanted columns, occurring as a result of glancing angle deposition, are considered as ellipsoids. Averaged shape parameters of these ellipsoids are defined using the density gradient tensor. Calculated values of difference of refractive index components of glancing angle deposited SiO2 films are in accordance with experiment.

1. Introduction

Glancing angle deposition (GLAD) is one of the technique for the fabrication of the anisotropic thin films with high porosity and low refractive index [1,2]. In this technique the incoming flux of the deposited atoms is directed almost parallel to the substrate surface. Due to density fluctuation in the deposited atoms flow and shadow effect [2], it results in formation of the different separate nanostructures - tree-like columns, slanted columns, chevron-like structures and so on – on the substrate. GLAD films are widely used in the optical coating due to low reflectance and their anisotropy properties [3-6].

The structural and optical properties of GLAD-films essentially depend on their fabrication conditions. Experimental investigation for the existing experimental techniques. On the other hand due to the progress in high performance computing, now it is possible to study thin films deposition process using the atomistic simulation [7-13]. In [10] the formation of slanted columnar structures in the GLAD SiO2 films under different deposition conditions is studied [10]. In the present work the anisotropy of the obtained in [10] clusters is investigated using the classical atomistic simulation and anisotropic Bruggeman effective medium theory [14]. The depolarizing factors defining the difference of the refractive index components are calculated based on the geometry parameters of the voids between the slanted columns forming the large-scale GLAD structure. The calculated values of the refractive index components are in accordance with experiment [5, 15].
Simulation is carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University [16].

2. Simulation method

The structures of GLAD silicon dioxide films are obtained using the classical MD method as described in [10]. Horizontal dimensions of the substrate are 20 nm and 60 nm, vertical thickness of the substrate is taken equal to 6 nm. The maximum value of deposited film thickness is about 45 nm. Scheme of GLAD deposition and sample of resulting film structure are shown in Fig.1.

![Scheme of GLAD deposition and Atomistic structure of GLAD SiO$_2$ film](image)

**Figure 1.** Tilt angle $\beta$, deposition angle $\alpha$ and atomistic structure of growing GLAD film [10]. Substrate atoms are painted as yellow (Si) and red (O), deposited atoms are painted as green (Si) and blue (O). Energy of the deposited Si atoms $E(Si) = 10$ eV.

Refractive index components $n_{x(y,z)}$ are calculated using the Maxwell relation between refractive index and dielectric constant $n^2 = \varepsilon$ and anisotropic Bruggeman effective medium theory for many-component materials [14]:

$$\sum_{i=1}^{n} f_i \frac{\varepsilon_i - \varepsilon_{e(x,y,z)}}{\varepsilon_{e(x,y,z)} + L_{a(x,y,z)}(\varepsilon_i - \varepsilon_{e(x,y,z)})} = 0 \quad (1),$$

where $f_i = V_i / V$ and $\varepsilon_i$ are the volume fraction and dielectric constant of $i$-th material, $\varepsilon_{e(x,y,z)}$ are the components of the effective dielectric constant, $L_{a(x,y,z)}$ are the depolarizing factors which are calculated as follows [14]:

$$L_{a(x,y,z)} = \frac{a_x a_y a_z}{2} \int_{-\infty}^{\infty} \frac{dx}{(x+a_x^2)(x+a_y^2)(x+a_z^2)} \quad (2),$$

where $a_x$, $a_y$ and $a_z$ are the averaged values of shapes parameters of ellipsoids. For the case of GLAD films Eq. (1) can be rewritten as follows:

$$f_i \frac{1 - \varepsilon_{e(x,y,z)}}{\varepsilon_{e(x,y,z)} + L_{a(x,y,z)}(1 - \varepsilon_{e(x,y,z)})} + (1 - f_i) \frac{\varepsilon_{e(y) - \varepsilon_{e(x,y,z)}}}{\varepsilon_{e(x,y,z)} + L_{a(x,y,z)}(\varepsilon_{e(y) - \varepsilon_{e(x,y,z)}})} = 0 \quad (3),$$
where \( \varepsilon_{df} = 2.22 \) [17] is the dielectric constant of dense silicon dioxide film, \( f_1 \) is the free volume fraction of GLAD film. Values of \( a_x \), \( a_y \) and \( a_z \) are calculated using the density gradient tensor [18]:

\[
\begin{pmatrix}
\rho_{xx} & \rho_{xy} & \rho_{xz} \\
\rho_{yx} & \rho_{yy} & \rho_{yz} \\
\rho_{zx} & \rho_{zy} & \rho_{zz}
\end{pmatrix} = (4),
\]

where \( \rho_{xy} \) is calculated as:

\[
\rho_{xy} = \frac{1}{V} \int \frac{\partial \rho(x,y,z)}{\partial x} \frac{\partial \rho(x,y,z)}{\partial y} dV = (5),
\]

where \( \rho(x,y,z) \) is the deposited film density, \( V \) is the film volume. Other components in (4) are defined on the similar way. The next relation can be used for the calculation of ellipsoid shape parameters [19]:

\[
\frac{\rho}{\rho_{av(x,y,z)}} = a_x^2(a_y^2,a_z^2)(6),
\]

where \( a \) is the numerical coefficient, \( \rho \) is the average film density. Eq. (6) provides only the values, proportional to the averaged ellipsoids shape parameters, but depolarizing factors in Eq. (2) depend only on the relation of these parameters. Indeed, using the substitution \( t = x a_x^2 \), we obtain for \( L_x \):

\[
L_x = \frac{1}{2} \int_0^{\pi} \frac{dt}{(t+1)^{3/2} \sqrt{(1+t(a_x/a_y)^2)(1+t(a_x/a_z)^2)}} (7),
\]

where \( t \) is the dimensionless integration variable. Similar equations can be obtained for other depolarizing factors. So the Eq. (6) is enough for the calculation of depolarizing factors.

To summarize, the procedure of the refractive index components calculation consists of the next steps:

1. Calculation of the free volume fraction \( f_1 \) as described in [20] or through the film density (see below).
2. Calculation of density gradient tensor components using Eq. (5) and diagonalization of tensor.
3. Calculation of averaged ellipsoids shape parameters and depolarizing factors using Eqs. (6, 7).
4. Calculation of \( \varepsilon_{(x,z)} \) and \( \varepsilon_{(y,z)} \) using Eq. (3) and Maxwell relation between refractive index and dielectric constant.

3. Results and discussion

To validate the described above method of \( n_{(x,z)} \) calculations the model structure is considered (Fig. 2). This structure consists of the same parallel layers of fused silica. Every layer has the next sizes: \( a_x = 2.5 \) nm, \( a_y = a_z = 25 \) nm. Distances between neighboring layers are the same.
Figure 2. The model structure used for the method validation.

The analytical structure for the case of unlimited in Y and Z layers can be derived as follows. Taking into account that \( \delta = a_x/a_s = a_y/a_s \rightarrow \infty \) and \( a_s = a_z \) the integrals (2) can be calculated as follows:

\[
L_y = \lim_{\varepsilon \rightarrow \infty} \frac{\int_0^\varepsilon \frac{dt}{\sqrt{(1+\delta^2)(1+t)^2}}} = 0; \quad L_z = \lim_{\varepsilon \rightarrow \infty} \frac{\int_0^{\delta^2}}{2} = 1
\] (8),

that coincides with known results [21,22]. Substituting these values to (3), we obtain:

\[
e_{\infty} = \frac{\varepsilon_x}{1-f_1\varepsilon_x}; \quad e_x = e_x = f_1 + (1-f_1)e_x
\] (9).

Free volume fraction \( f_1 \) for this model task is equal \( f_1 = (28-7a_s)/28 = 0.375 \) (see Fig. 2). As it follows from (9):

\[
e_x = 1.52, \quad e_y = e_z = 1.76
\] (10).

These values are considered as reference for the presented method.

Results of the dielectric constant components calculations for the model structure are presented in Tab. 1. Value of \( f_1 \) is equal 0.375. As it shown in Tab. 1, values of \( e_{x(1,2)} \) essentially depend on the differentiation step \( h \). Increase of \( h \) results in the reduce of the difference between the numerical and analytical values of \( e_{x(1,2)} \) (10). It can be explained as follows. If the \( h \) value is about of the chemical bond length \( \sim 0.15 \) nm, the number of atoms changes noticeably from one integration cell with volume \( h^3 \) to another. These density fluctuations, related to the details of the atomistic structure, contribute to the derivatives. Increase of \( h \) reduces of this contribution. At the same time the thickness of the slanted columns and the distances between them are about of several nanometers. Thus increase of \( h \) to \( \sim 1 \) nm removes the atomistic structure fluctuations from the derivatives and takes into account the large-scale heterogeneities like slanted columns. This is confirmed by the growth of \( a_x/a_s \) and \( a_y/a_s \) relations with increase of \( h \). Indeed neglecting the fluctuations of the atomistic level, only the density dependence on \( x \) coordinate remains (Fig. 2). In frame of the Bruggeman effective medium theory this structure corresponds to a set of ellipsoids strongly elongated in \( Y \) and \( Z \) directions so \( a_x >> a_s \) and \( a_y >> a_s \).

Table 1. Dependence of the parameters of the Bruggeman effective medium theory on the differentiation step \( h \) in Eq. (5). Definitions of other values see the text above.

| h, nm | 0.2 | 0.5 | 0.8 | 1.0 | 1.5 | 2.0 |
|-------|-----|-----|-----|-----|-----|-----|
| \(a_x/a_s\) | 2.8 | 4.2 | 8.2 | 18  | 30  | 32  |
| \(a_y/a_s\) | 1.9 | 1.8 | 3.4 | 7.4 | 12  | 13  |
| \(L_x\) | 0.56 | 0.59 | 0.74 | 0.86 | 0.91 | 0.91 |
| \(L_y\) | 0.28 | 0.31 | 0.20 | 0.11 | 0.07 | 0.07 |
| \(L_z\) | 0.16 | 0.1  | 0.06 | 0.03 | 0.02 | 0.02 |
| \(e_x\) | 1.64 | 1.63 | 1.59 | 1.56 | 1.55 | 1.54 |
| \(e_y\) | 1.70 | 1.69 | 1.72 | 1.74 | 1.75 | 1.75 |
| \(e_z\) | 1.73 | 1.74 | 1.75 | 1.76 | 1.76 | 1.76 |

Value of free volume fraction \( f_1 \) is calculated using two methods. First of them is based on the film density dependence on the deposition angle \( \rho(\alpha) \):

\[
f_1(\alpha) = 1 - \rho(\alpha)/\rho(0)
\] (11).
It’s assumed in (11) that the normally deposited film (\(\alpha = 0\)) has no free volume and the density inside slanted column in GLAD films is equal to \(\rho(0)\).

The second method is based on the calculation of film porosity using the atomic radii as described in [19]. Van der Waals radii of oxygen and silicon atoms are taken equal to \(R_{vdW}(O) = 0.152\) nm [23] and \(R_{vdW}(Si) = 0.21\) nm [24], ionic radii of two-coordinated oxygen and four-coordinated silicon are equal to \(R_i(Si) = 0.026\) nm and \(R_i(O) = 0.135\) nm [25]. The volume fraction of pores \(F(\alpha)\), designated in [20] as \(f(R = 0)\) is calculated for both types of radii for specified values of the deposition angles \(\alpha\). The free volume fraction \(f_i\) is calculated as follows:

\[
f_i(\alpha) = F(\alpha) - F(0) \quad (12).
\]

In (12) as well as in (11) it’s assumed that the normally deposited film has no free volume that should be take into account in Bruggeman effective medium theory. Indeed the free volume in the normally deposited films is formed by the small pores having sizes about of 0,1 nm [20]. The set of these pores is not considered as a special medium in the Bruggeman theory.

All values required for \(f_i(\alpha)\) calculation are presented in Tab.2.

**Table 2.** Dependencies of the film density \(\rho\) (g/cm\(^3\)) and volume fraction of pores \(F_{vdW}(\alpha)\) (Van der Waals radii) and \(F(\alpha)\) (ionic radii) on the deposition angle \(\alpha\) (grad).

| \(\alpha\) | 0   | 30  | 60  | 80  |
|------------|-----|-----|-----|-----|
| \(F_{vdW}(\alpha)\) | 0,16 | 0,16 | 0,32 | 0,57 |
| \(F(\alpha)\) | 0,40 | 0,40 | 0,52 | 0,71 |
| \(\rho(\alpha)\) | 2,40 | 2,40 | 1,95 | 1,22 |
| \(f_i, Eq.(11)\) | 0   | 0   | 0,19 | 0,49 |
| \(f_i, Eq.(12), vdW\) | 0   | 0   | 0,16 | 0,41 |
| \(f_i, Eq.(12), ionic\) | 0   | 0   | 0,12 | 0,31 |

Results of the model parameters and refractive index calculations are presented in Tab. 3. Increase of deposition angle \(\alpha\) results in the decrease of the refractive index and increase of the free volume fraction and anisotropy effects. For all cases the \(n_z\) component, corresponded to the axis \(Z\) perpendicular to the surface of the slanted column (Fig. 1), is less than \(n_x\) and \(n_y\) component. This result is the same as that obtained for the model structure (Fig. 2). The difference of the refractive index components varies from a few thousandths to a few hundredths.

The maximum \(n_z - n_x\) values (last row in Tab. 3) are obtained for the free volume fraction calculated through film density, Eq. (11). In spite of noticeable difference in \(F_{vdW}(\alpha)\) and \(F(\alpha)\) values (Tab. 2) the refractive index components differ slightly for the cases of ionic radii and Van der Waals radii.

Experimental values of the refractive index components of SiO\(_2\) GLAD films are shown in Fig. 3 in Ref. [5]: \(n_z = 1,23; n_x = 1,29; n_y = 1,28\) (\(\alpha = 80^\circ\)) and \(n_z = 1,39; n_x = n_y = 1,42\) (\(\alpha = 60^\circ\)). The method of the free volume fraction definition based on the Eq. (11) ensures the minimal difference between experimental and calculated \(n_{z(x,y)}\) values. For both deposition angles calculated \(n_{z(x,y)}\) values are less than experimental ones. The possible reason for it is the difference in the free volume fraction values: \(f_i = 0,1 (0,4)\) for \(\alpha = 60^\circ(80^\circ)\) in [5] and \(f_i = 0,19(0,49)\) in present work (Tab. 3). Both free volume fraction values are in the interval of the experimental and simulation results [26,27].

The \(\Delta n\) values are equal to 0,03 and 0,05 for \(\alpha = 60^\circ\) and \(\alpha = 80^\circ\) respectively, if Eq. (11) is used for \(f_i\) calculations (Tab. 3). These values coincide with the experimental ones [5]. As expected, growth of the deposition angle results in the increase of \(\Delta n\) values due to increase of the free volume fraction, see Eq. (3).
Table 3. Parameters of the Bruggeman effective medium theory and main components of refractive index of GLAD SiO$_2$ films. Differentiation step $h$ is equal to 1 nm.

| $\alpha$, $^\circ$ | 60     | 80     |
|-------------------|--------|--------|
| $f_1$             | 0.16$^1$| 0.12$^2$| 0.19$^3$| 0.31$^{1,2}$| 0.49$^4$|
| $a_x/a_z$         | 3.9    | 4.6    | 4.6    | 3.2    | 3.7    |
| $a_y/a_z$         | 2.4    | 2.4    | 2.4    | 2.1    | 2.1    |
| $L_x$             | 0.12   | 0.10   | 0.10   | 0.15   | 0.13   |
| $L_y$             | 0.25   | 0.25   | 0.25   | 0.26   | 0.27   |
| $L_z$             | 0.63   | 0.65   | 0.65   | 0.59   | 0.60   |
| $n_x$             | 1,418  | 1,437  | 1,406  | 1,347  | 1,262  |
| $n_y$             | 1,413  | 1,433  | 1,399  | 1,339  | 1,248  |
| $n_z$             | 1,393  | 1,415  | 1,374  | 1,311  | 1,215  |
| $n_x - n_y$       | 0.005  | 0.004  | 0.007  | 0.008  | 0.014  |
| $n_x - n_z$       | 0.025  | 0.018  | 0.032  | 0.036  | 0.047  |

$^1$Eq. (12), van der Waals radii;  
$^2$Eq. (12) ionic radii;  
$^3$Eq. (11).

4. Conclusions

Anisotropy of atomistic clusters of SiO$_2$ GLAD films, obtained in molecular dynamics simulation of the deposition process, is investigated using Bruggeman effective medium theory. The voids between the slanted column structures are considered as ellipsoids having different shapes parameters. Average values of these parameters are calculated using the density gradient tensor. Values of difference of main components of refractive index $\Delta n$ are equal 0.03 and 0.05 for deposition angles 60$^\circ$ and 80$^\circ$, if the free volume fraction is calculated using the dependence of film density on the deposition angle. The obtained values of $\Delta n$ coincide with experiment.

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References

[1] Robbie K, Brett M J, Lakhtakia A 1996 *Nature* **384** 616.
[2] Hawkeye M M, Brett M J 2007 *J. of Vac. Sci and Techn.* **25** 1317.
[3] Zhao Y P, Ye D.X, Wang P I, Wang G C, Lu T M 2002 *Int. J. Nanosci.* **1** 87.
[4] Woo S.-H., Park Y J, Chang D H, Sobahan K M A, Hwangbo C K 2007 *J. Korean Phys. Soc.* **51** 1501.
[5] Tkachenko V, Marino A, Otón E, Bennis N, Otón J M 2016 *Beilstein J. Nanotechnol.* **7**, 1743.
[6] Trottier-Lapointe W, Zabeida O, Schmitt T, Martinu L 2016 *Appl. Opt.* **55** 8796.
[7] Smy T, Vick D, Brett M J, Dew S K, Wu A T, Sit J C, K.D. Harris K D 2000 *J. Of Vac. Sci. and Techn. A* **18** 2507.
[8] Grüner C, Liedtke S, Bauer J, Mayr S G 2018 *ACS Appl. Nano Mat.* **1** 1370.
[9] Backholm M, Foss M, Nordlund K 2012 *Nanotechnology* **23** 385708.
[10] Grigoriev F V, Sulimov V B, Tikhonravov A V 2019 *J. of N.-Cr. Sol.* **512** 98.
[11] Grigoriev F V, Sulimov A V, Katkova E V, Kochikov I V, Kondakova O A, Sulimov V B, Tikhonravov A V 2017 *Applied Optics* **56** C87.
[12] Grigoriev F V, Sulimov A V, Katkova E V, Kochikov I V, Kondakova O A, Sulimov V B, Tikhonravov A V 2016 *J. of Non-Cr. Sol.* **448** 1

[13] Grigoriev F V, Sulimov A V, Katkova E V, Kochikov I V, Kondakova O A, Sulimov V B, Tikhonravov A V 2016 *Opt. Mat. Express* **6** 3960.

[14] Schmidt D, Schubert M 2013 *J. Appl. Phys.* **114** 083510.

[15] Hawkeye M M, Taschuk M T, Brett M J Glancing Angle Deposition of Thin Films: Engineering the Nanoscale. John Wiley & Sons, Jul 3, 2014 - Technology & Engineering - 320 pages

[16] Voevodin Vl, Antonov A, Nikitenko D, Shvets P, Sobolev S, Sidorov I, Stefanov K, Voevodin Vad, Zhumatyi S 2019 *Supercomputing Frontiers and Innovations* **6** 4.

[17] Handbook of Optical Materials, Editor-in-Chief: Marvin J. Weber. The CRC Press Laser and Optical Science and Technology Series. 2003, P.499.

[18] S. Arseneau, *Junction Analysis: Representing Junctions through Asymmetric Tensor Diffusion* (VDM Verlag Dr. Müller e.K., 2008).

[19] Badorreck H, Steinecke M, Jensen L, Ristau D, Jupé M, Müller J, Tonneau R, Moskovkin P, Lucas S, Pflug A, Grinevičiūtė L, Selskis A, Tolenis 2019 *Opt. Express* **27** 22209.

[20] Grigoriev F V, Sulimov V B, Tikhonravov AV 2019 *Moscow University Physics Bulletin, 74*, 171.

[21] Osborn J A 1945 *Phys. Rev.* **67** 351.

[22] Stoner E C 1945 *Phil. Mag.* **36** 803.

[23] Bondi A 1964 *J. Phys. Chem.* **68** 441.

[24] Allinger N L 1976 *Adv. Phys. Org. Chem.* **13** 1.

[25] Shannon R D 1976 *Acta Crystallogr. A* **32**, 751.

[26] Yang S, Zhang Y 2013 *Surf. Interface Anal.* **45**, 1690.

[27] Poxson D J, Mont F W, Schubert M F, Kim J K, Schubert E F 2008 *Appl. Phys. Lett.* **93**, 101914.