

Modeling of Oxynitride-Si System Based on Reflected Spectra

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ABSTRACT

Using *ab initio* molecular dynamics simulation with simultaneous quantum chemical calculations we propose a new experimental method of contact-less control of the O/N ratio in SiON films on Si<111> surfaces. The proposed method consists of direct measurements of reflected light coefficients for the parallel R_p and perpendicular R_s light polarizations in relation to the Si<111> plane. We have shown that the spectral dependence of the anisotropic ratio $P=R_s/R_p$ is closely connected to the O/N ratio. Independently performed experimental spectra measurements correspond well with experimental data. We demonstrate significant advantages over ellipsometry, XPS and other measurements both in precision as well as in technical implementation.

Keywords: amorphous thin films; silicon oxynitride.

INTRODUCTION

Due to their technological importance, silicon oxynitrides have, in recent years, been the subject of increasing research interest [1]. A central point here remains the problem of rapid determination of the O/N (Oxygen/Nitrogen) ratio. Traditional methods have a major drawback in their low sensitivity to the above mentioned parameter. We performed *ab initio* molecular dynamics simulations of the SiON-Si<111> system in order to find a method more sensitive to the O/N ratio.

MATHEMATICAL MODELLING AND SIMULATIONS

There are many papers concerning *ab initio* molecular dynamics simulations of different disorder systems [e.g. 2,3]. We therefore only briefly mention mathematical simulation procedure for the determination of optical response functions.

To simulate the behavior of the response functions in the SiON-Si<111> system, we used the hybrid Becke's molecular dynamics geometry optimization method [4], involving a semi-empirical contribution of the „exact” exchange ExHF (i.e. Hartree-Fock-type, but based on Kohn-Sham orbitals) and of the exchange energy EgLSDA in the density functional theory (DFT), together with a gradient-corrected correlation functional ECLSDA. The DFT calculations were performed with the GAUSSIAN94

program [5], using the polarized-correlated double-basis sets (cc-Pvdz [6]). The main advantage of this method is the very fast convergence of the eigenvalues with respect to the size of the basis sets.

A typical example of a cluster optimized in such a way is presented in Fig. 1.

Our calculations have shown that among more than thirty calculated parameters (such as density of states, structural factors, Debye-Waller broadening, photo-ionizations,

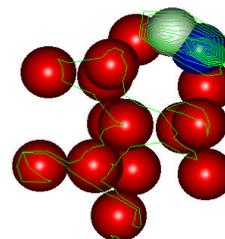


Fig. 1. An example of appearance of charge density non-centrosymmetry in the SiON films on the Si<111> surfaces.

Auger cross-section, dielectric susceptibilities, etc) the most sensitive to variation of the O/N ratio is spectral dependency of polarization ratio $P=R_s/R_p$. The quantum chemistry calculations were carried out self-consistently after separation of the electron and phonon degrees of freedom. We carried out more robust theoretical quantum chemical calculations in order to explain our experimental data and to clarify the associated physical mechanisms. The main principles of our approach can be summarized as follows:

- *ab initio* calculations of the electronic structure,
- molecular dynamics geometry optimization,
- contribution of the electron-vibration interaction including anharmonic corrections,
- contribution of the inter-cluster interactions.

To determine the density of quantum states, we calculated electron states and the appropriate optical transitions for the most important cation-anion polyhedral clusters, particularly the Si-N and Si-O clusters before and after UV-light illumination. The geometry optimization procedure was identical to that described above. At the same time, we looked for a potential energy minimum, taking into account the discharged intermolecular interaction before and after UV-illumination. This was based on changes of Fermi

energy corresponding to variations of the photo-induced carrier concentrations and resonance vibrations.

The molecular orbital (MO) electronic structure (energy molecular levels and corresponding MO wave-functions) were obtained self-consistently using a standard Linear Muffin Tin Orbitals (LMTO) technique in atomic sphere approximation. The necessary quasi-Brillouin zone integrals were calculated using linear tetrahedra with a grid of 762 \mathbf{k} -points in an irreducible part of the quasi-Brillouin zone. The equilibrium atom positions were obtained on the basis of the condition for the minimum of electron charge density functional (\mathbf{r}). The quantum chemistry calculations were carried out self-consistently after separation of the electron and vibration degrees of freedom. The Schroedinger equation for pure vibration motion can be expressed in a harmonic approximation

$$\frac{d^2}{dQ_k^2} \psi_k + \left(4\pi^2 \mu_k h^{-2} E_k^2 \right) \psi_k = 0 \quad (1)$$

where ψ_k is the wave-function corresponding to the k -th normal coordinate, and Q_k and μ_k denote the reduced coordinates and mass respectively of the nuclei involved in the k -th vibration mode. The eigen-energy of the k -th vibration mode is expressed as

$$E_k(\nu_k) = 2E_{k0} \nu_k + \frac{1}{2} \quad (2)$$

where

$$E_{k0} = \frac{h}{4\pi} \frac{f_k}{\mu_k} \quad (3)$$

denotes the zero-point motion energy, f_k is the force constants and $\nu_k = 0, 1, 2, \dots$ refers to the vibration quantum number associated with the following wave-function

$$\psi_k(Q_k) = \frac{2E_{k0}}{\pi} \frac{1}{4} \frac{2^{\nu_k}}{\nu_k!} \frac{1}{2} e^{-E_{k0} Q_k^2} H_{\nu_k} \left(\frac{Q_k}{E_{k0}} \right) \quad (4)$$

where $H(x)$ is the Hermite polynomial. It is clear therefore that any change in the clusters may be described as a local perturbation.

At the first stage, the electron-phonon interaction potential was calculated within a non-linear approximation

$$V_{e-ph}(\mathbf{r}_i) = e^2 \sum_{m's} M_{ms}^{-\frac{1}{2}} \left[\sum_{ms} (\mathbf{r}_s - \mathbf{u}_{ms}) \mathbf{r}_s - \mathbf{u}_{ms} \right]^{-3} - \sum_{m's} Z_{m's} \left(\mathbf{r}_s - \mathbf{u}_{m's} \right) \mathbf{r}_s - \mathbf{u}_{m's} \left| \right|^{-3} \quad (5)$$

where M_{ms} and eZ_{ms} represent the effective ionic mass and charge, respectively (corresponding ions are numbered by m and s). The $\mathbf{u}_{ms,m's}$ vector is the measure of the relative displacement of two ions from their equilibrium positions \mathbf{r}_s and $\mathbf{r}_{s'}$. The probability of a one-phonon transition induced by the vibration of frequency ν_k is equal to

$$W^-(\nu_k) = 4 \frac{h}{2\pi} c^{-3} H^{-1} g^{-1}(\mathbf{r}_i) (E_{el} - \nu_k)^2 B^-(\nu_k) \quad (6)$$

where ϵ_{ξ} and ϵ_{η} denote lower and upper electron MO energy levels, respectively; H is the sum of the level widths; E_{el} represents the energy of the intermolecular transition; ν_k denotes the k -th vibration energy and $g(\mathbf{r}_i)$ is the degree of degeneration of the corresponding electron energy levels. The parameter $B^-(\nu_k)$ is equal to

$$B^-(\nu_k) = \sum_{\xi}^{g(\eta)} \sum_{\eta}^{g(\xi)} \left\{ \langle \varphi | \mathbf{d} | \xi \rangle \langle \xi | V_{e-ph}(\mathbf{r}_i) | \eta \rangle + \langle \varphi | \mathbf{d} | \eta \rangle \langle \eta | V_{e-ph}(\mathbf{r}_i) | \xi \rangle \right\} \left(E_{\xi} - E_{\eta} + \nu_k \right)^{-1} \left(E_{\xi} - E_{\eta} - \nu_k \right)^{-1} \quad (7)$$

where ξ denotes a virtual intermediate MO electron state, \mathbf{d} is an electric dipole moment for the given optical transition. The summation is made for all degenerated initial and final states. The symbol $\langle \dots \rangle$ denotes the average with respect to occupation numbers of the quasi-phonon states for quasi-phonons with frequency ν_k .

Our calculations suggest that Si-N clusters play a dominant role in the anisotropy of optical susceptibilities since the electronic charge density was drastically redistributed after UV-excitation, while the changes were minute for other clusters (particularly Si-O and Si-Si). We can therefore conclude that the Si-N clusters are responsible for the appearance of local charge density anisotropy of the electronic charge distribution. This is extremely important because it leads to the appearance of the non-linear optical susceptibilities observed.

On the other hand, the symmetric vibrations included in the electron-phonon interaction (Eq. 5) can lead to the following normal coordinates

$$B^-(\nu_k) = C_{\eta\xi}^{\nu}(\nu_k) C_{\eta\xi}^{\nu}(\nu_k) m G^{\nu}(\nu_k, \nu_k) \quad (8)$$

where $G^{\nu}(\mathbf{r})$ is the Green function (ν and ν' are numbers of coordination spheres and ν corresponds to the direction of effective electron-phonon modes) defined as

$$G^{\nu}(\nu_k) = \left\{ \langle \eta | V_{e-ph}(\mathbf{r}_i) | \varphi \rangle \langle \varphi | \mathbf{d} | \xi \rangle + \langle \eta | \mathbf{d} | \varphi \rangle \langle \varphi | V_{e-ph}(\mathbf{r}_i) | \xi \rangle \right\} (E_{\xi} - E_{\eta})^{-1} \quad (9)$$

The resulting expression is as follows

$$G^{(1)}(\mathbf{k}, \omega) = K^{(1)}(\mathbf{k}) K^{(0)}(\mathbf{k}) \left(\frac{1}{\omega - \omega_k - i\delta} \right)^{-1} \quad (10)$$

where coordinates $K(\mathbf{r})$ are obtained for a given vibration type after taking an average for all electron states. To include the lattice deformations in the Green function, we took into account a deformation localization that allowed us to use the Dyson relations. The deformation potential and corresponding charge defect perturbation determine a potential operator U , and

$$G^{(1)}(\mathbf{k}) = G^{(0)}(\mathbf{k}) + G^{(0)}(\mathbf{k}) U G^{(1)}(\mathbf{k}) \quad (11)$$

where $G^{(0)}(\mathbf{k})$ and $G^{(1)}(\mathbf{k})$ are the Green functions for an ideal system and a system with defects, respectively. Dependencies between a real and imaginary part of the Green function were obtained using Kramers-Kronig dispersion relations.

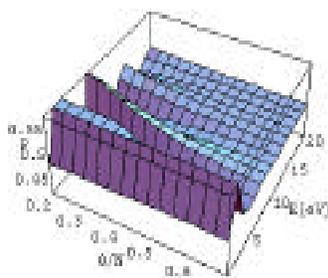


Fig. 2. Calculated spectral dependence of the P versus O/N ratio

We took into account both harmonic as well as anharmonic electron-phonon interactions using a Green function approach with simultaneous resolving of Dyson equations. A more detailed calculation of the optical anisotropy ratio is presented in the References [7,8].

To estimate the anisotropic ratio, we made calculations of the real and imaginary part of the dielectric susceptibilities using the above-mentioned technique. Then, by applying the Kramers-Kronig relations we evaluated the corresponding ratio for the reflection coefficients for two polarizations: parallel and perpendicular.

Typical calculated spectral dependency of the P versus O/N ratio are presented in Fig. 2. With increasing O/N ratio, we observe changes of the polarization ratio P.

EXPERIMENTAL TECHNIQUE

The SiON films on the Si<111> surfaces with different O/N ratio were prepared using the following technology: the entire process was carried out using a growth rate, dependent on the O/N ratio, chosen in accordance with the Habraken rule. The specimen was

mounted on a manipulator and its temperature was varied between 120 K and 1450 K. We applied the EXAFS method to control stoichiometry of the films. Energy flux was changed within the range 280 - 1500 eV. Using a mathematical algorithm, we separated N-K and O-K fluorescence signals.

We measured photo-electron spectra of Si-2p, N-1s and O-1s levels in order to link changes in binding energy and intensity to changes in the geometric structure as determined by EXAFS. This method is usually carried out using X-ray absorption or transmission spectroscopy. Due to insignificant energetic separation, the O-K absorption overlapped the N-K absorption fine structure. For further analysis, it is highly desirable to gain distinct spectra. We, therefore, measured the fluorescence yield as a function of incident photon energy ranging from 350 eV to 1050 eV. The signal of the fluorescence detector was sampled in a multi-channel analyzer and divided into two channel windows containing different amounts of the N-K and O-K fluorescence signal. To obtain accurate fits, it was necessary to consider the first and second coordination sphere in the calculation. This underlines the importance of the interaction of the second neighbors.

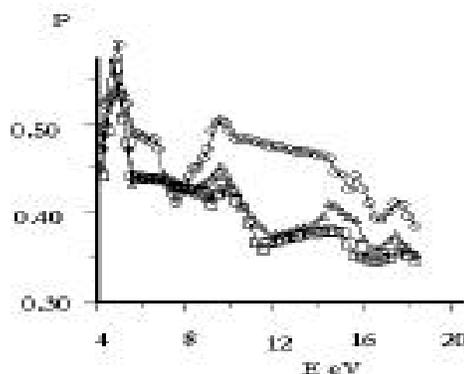


Fig. 3. Measured spectral dependencies of the P for specimens with different O/N ratio: o – 0.3; - - 0.45; . . . 0.6.

The samples investigated were in the form of plates with thickness of 10 nm to 30 nm, and their surface area was about 1 cm². Measurements of spectral dependencies of the polarization ratio P (between the intensities for two light polarizations) were achieved in the spectral range 2.5-15 eV, using UV spectrophotometer Seya-Numioka with resolution up to 7 nm/mm. The incident angle was less than 7°. In order to avoid unhomogeneity of the specimens, all the measurements were taken in more than 40 points of every specimen. From experimental data (see Fig. 3), one can see a similarity to the theoretically predicted P (see Fig. 2) spectral behavior.

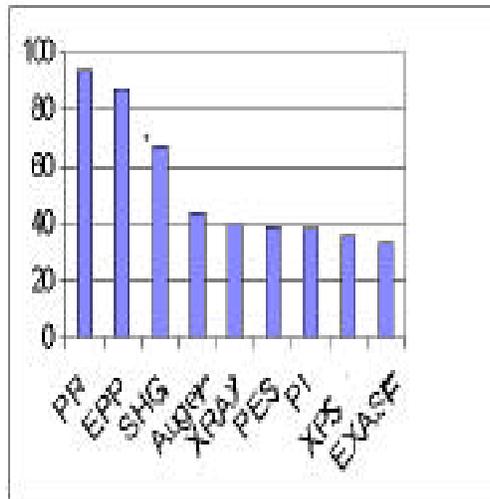


Fig. 4. Comparison of sensitivity of the different methods towards the O/N ratio.

The data unambiguously show agreement between the calculated and experimental behavior of the polarized reflected anisotropy. The experimental data, as well as theoretical results, confirm the key role of the Si-N chemical bonds contributing to the output anisotropy of the reflected signal. Several discrepancies reflect a surface non-homogeneity of the investigated specimens and can be ignored.

The simulations we carried out show that the main parameter sensitive to the N/O ratio is the charge density anisotropy (see Fig.1).

MAIN RESULTS AND DISCUSSION

In Fig. 4 we present the effective parameter of sensitivity consisting of relative changes to the detected signals under the influence of changes to the O/N ratio.

We have demonstrated an essential advantage of polarized reflection spectra PR over other methods. Our mathematical simulations have shown that the main source of the high level of accuracy of the O/N ratio determination is the variation of O/N anisotropy particularly sensitive to the macroreflectivity for different crystallography directions. The high degree of correspondence between the experimental and theoretical data indicates the efficiency of our approach to the non-destructive control of different physical-parameters in the SiON-Si<111> systems. The proposed method can be applied not only to SiON films on the Si<111> surfaces but also to other semiconducting materials, particularly to SiC nanoclusters. The latter are very sensitive to anisotropy in the electronic charge density distribution. In contrast to ellipsometry measurements, we are able to achieve control of the integrated surfaces and obtain information concerning the distribution of the different chemical components, both throughout the specimen depth as well as for the different localized states.

CONCLUSIONS

Using complex experimental spectroscopic and theoretical quantum chemical approaches, we have demonstrated the efficiency of using polarized reflection spectra to determine the O/N ratio in SiON films on Si<111> surfaces. The obtained data reflect the appearance of anisotropy due to the asymmetry of the charge density distribution with the increase of nitrogen content. We have demonstrated significantly higher sensitivity of the proposed method compared to traditional methods.

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