OPTICS, LASERS, AND QUANTUM ELECTRONICS

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DESTRUCTION
OF NANO-INHOMOGENEITIES OF THE SURFACE
OF DIELECTRICS USING THE OPTICAL NEAR-FIELD

The destruction of surface nano-inhomogeneities of a quartz substrate using the optical near-field dipole-dipole interaction of atomic chlorine with SiO_2 is studied. A method to obtain atomic chlorine by the local photodissociation of molecular chlorine by the optical near-field of the quartz substrate nano-inhomogeneities is proposed. The polarization of chlorine atoms and SiO_2 by means of an evanescent wave, which is generated on the substrate surface, is investigated. A method is proposed to obtain the most optimal orientation of the dipoles of atomic chlorine and SiO_2, using the features of the optical near-field, to maximally efficiently destroy the quartz substrate nano-inhomogeneities. The application of the composite quasiparticle model describing the optical near-field interaction of dipoles is considered.

K e y w o r d s: subnano-polishing, destruction, dipole-dipole interaction, photodissociation, optical near-field, evanescent wave.

1. Introduction

Optical elements (for example, lenses, prisms, mirrors) are widely used in most optical devices: lasers, gyroscopes, physical field sensors, *etc.* An important characteristic of the above-mentioned elements is the degree of inhomogeneity (roughness) of the surface, on which the accuracy of measuring devices depends. The traditional methods such as the chemical mechanical planarization [1], whose use reduces the surface roughness and thus improves its quality are well known. At the same time, these methods do not allow reducing the nano-defects of the surface to a subnanometric scale. This can be achieved by using an optical near-field (NF), due to which the surface nano-inhomogeneities can be destructed. The following methods of optical near-field

subnano-polishing have been most developed in recent years:

• in 2010 [2], the polishing of the quartz substrate with chlorine under the illumination with the green laser radiation from above without focusing;

• in 2013 [3], the polishing of translucent substrates using a light-absorbing film;

• in 2014 [4], the selective etching of surfaces using chlorine and chlorine-containing gases (boron trichloride and hydrogen chloride);

• in 2015 [5], the surface planarization using reaction gases;

• in 2016 [6], the polishing of the surface of dielectrics (such as glass, plastic, silicon wafer, diamond, and gallium nitride) using reaction solutions.

Thus, the opportunities to destroy surface nano-inhomogeneities using the optical NF determine the relevance of this study and the further prospects for the practical use of the results obtained.

2. Theoretical Insights and an Idea of Experiment

In a vacuum chamber, we placed the quartz substrate with nanometer scale roughness, to which a total internal reflection (TIR) prism made of quartz, is attached from below (Fig. 1). The space between the substrate and the prism is filled with an immersion liquid to avoid the re-reflection. Conventional molecular chlorine Cl_2, chemical activity of which is not sufficient [2] to react with quartz at room tempera-
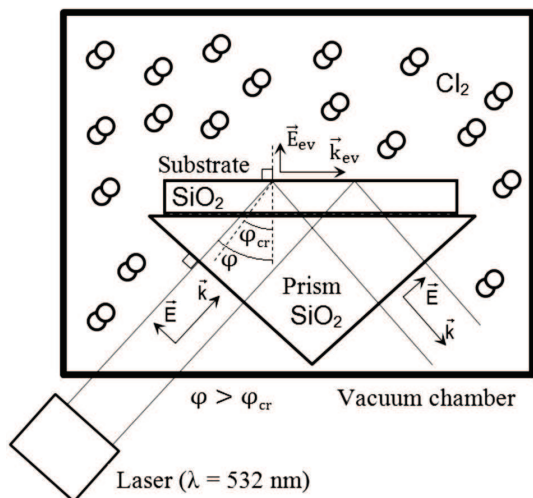

Fig. 1. Scheme of the experimental setup ($\mathbf{k}_{ev}$ and $\mathbf{E}_{ev}$ are wave vector and the electric field strength of the evanescent wave, respectively, φ is the angle of incidence of the laser radiation on the lower surface of a quartz substrate, φ_{cr} is the critical angle)
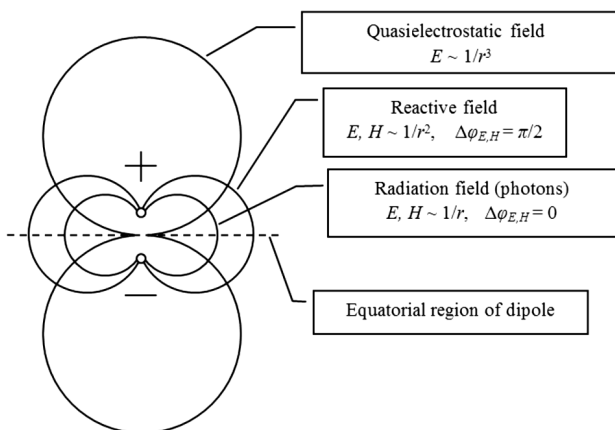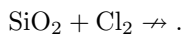

**Fig. 2.** Directional diagrams of three components of the electromagnetic field generated by the dipole

ture, is launched into the chamber:

$$SiO_2 + Cl_2 \nrightarrow \ .$$

The lower edge of the TIR prism is irradiated normally by the DPSS laser radiation ($\lambda = 532$ nm), which causes it to fall on the substrate from below at the TIR angle. Above the upper substrate surface at a distance $< \lambda/2\pi$, an evanescent wave is formed, which propagates only along a portion of the surface irradiated with a laser. The evanescent wave polarizes Cl_2 and SiO_2. The resulting dipoles generate all three components of the electromagnetic field [7] (Fig. 2). The field of the evanescent wave is very inhomogeneous and exponentially extinct, when it moves away from the substrate surface. Therefore, it attracts Cl_2 to the quartz substrate surface.

It can be seen from the plots (Fig. 3) that the quasielectrostatic component $\sim 1/r^3$ is the strongest in the near zone. Its value is several orders greater than the reactive field $\sim 1/r^2$ or especially than the radiation field $\sim 1/r$, which dominates only in the far zone.

The component $\sim 1/r^3$ of the SiO_2 dipole radiation causes the dissociation of molecular chlorine [2]:

$$Cl_2 \xrightarrow{\text{NF}} 2Cl.$$
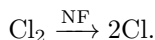
Thus, the molecular chlorine Cl_2, getting into the NF, dissociates to the more chemically active atomic chlorine Cl. This process is irreversible in NF. In turn, atomic chlorine is also polarized by the evanescent wave, forming a dipole, which is attracted to the SiO_2 dipole of the nano-inhomogeneity peak.

The vector of the electric field strength of the evanescent wave is always directed orthogonally to the surface plane (Fig. 1). The electric dipole moments of Cl and SiO_2 are oriented in the same direction ($\mathbf{E}_{ev}$) along the same straight line and unlike poles to each other (Fig. 4). In this case, the interaction of Cl and SiO_2 dipoles is due to the strongest near-field component $\sim 1/r^3$, unlike the previous experiments of photochemical subnano-polishing [2–6], where the substrate was irradiated from above, orthogonally to the surface plane, and the dipoles of Cl and SiO_2 were oriented in parallel, equatorial regions to each other (Fig. 5). With such a mutual arrangement of dipoles, their interaction was due to the much weaker near-field component $\sim 1/r^2$. In addition, the like poles of the dipoles were located next to
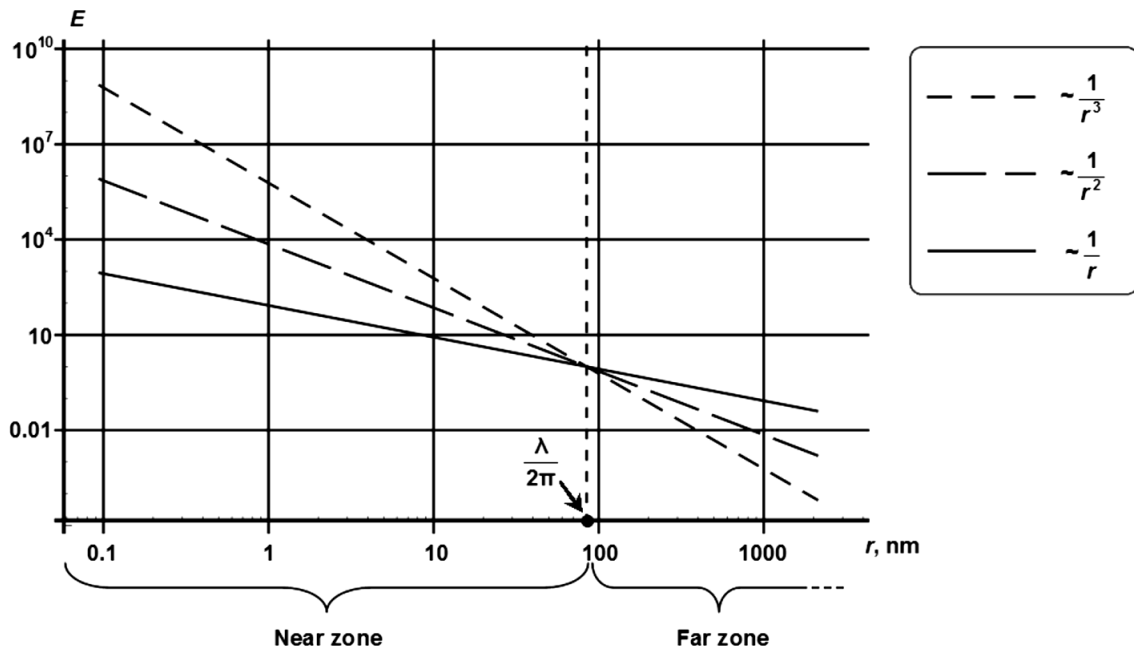
Fig. 3. Plots of the dependence of the relative values of the electric field strength on the distance between interacting dipoles for three components of the electric field (both axes have a logarithmic scale)
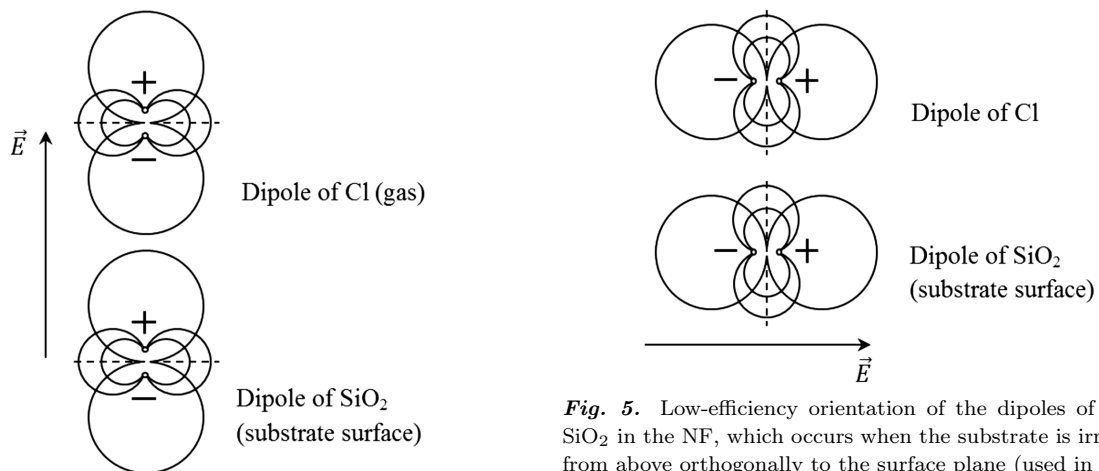

Fig. 4. Most optimal orientation of the dipoles of Cl and SiO$_2$ obtained by using the evanescent wave formed due to TIR (used in this work)

Fig. 5. Low-efficiency orientation of the dipoles of Cl and SiO$_2$ in the NF, which occurs when the substrate is irradiated from above orthogonally to the surface plane (used in [2–6])

each other, which further pushed apart dipoles and reduced the intensity of their interaction.

Thus, the orientation of dipoles in this study is the most optimal of all possible ones. As a result of the reaction of atomic chlorine with nano-inhomogeneities of the quartz substrate, gaseous substances (including chlorine compounds) are formed with a density lower than the density of molecular chlorine, due to which they are expelled from the reaction zone. For example, due to the reaction with the formation of silicon tetrachloride, the roughness of the quartz substrate is etched:

$$SiO_2 + 4Cl \xrightarrow{\text{NF}} SiCl_4\uparrow + O_2\uparrow.$$
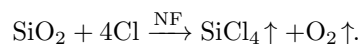
As well, the noteworthy (non-standard) feature of this reaction is that each SiO$_2$ fragment of the quartz

substrate nano-inhomogeneity must interact with four atoms of atomic chlorine before they interact with one another (forming two Cl_2 molecules), which is possible only in the NF. Thus, if the laser is turned off, and the NF is removed in this way, then four chlorine atoms surrounding the SiO_2 fragment, without having to react with it, firstly interact with each other and form two molecules of ordinary chlorine Cl_2, which does not interact with quartz. Therefore, the process of photochemical subnano-polishing will stop.

3. Near-Field Quasiparticle Model

The exciton-phonon polariton model is proposed in Ref. [8] as a model of quasiparticle in the optical near-field probe for studying the physical mechanisms of chemical vapor deposition via an optical near-field.

In our study, to generate an optical NF on the quartz substrate surface, instead of a fiber probe, an evanescent wave traveling along the substrate surface in the region illuminated by a laser is uses. But since the generation of an optical near-field will occur at the peaks of nano-inhomogeneities of the substrate surface, the exciton-phonon polariton model can be used here. Cl_2 molecules polarized by the NF are attracted by Coulomb forces like optical tweezers to the region of the largest NF gradient concentrated at the peaks of nano-inhomogeneities of the substrate surface. Suppose that the exciton-phonon polaritons are created at the peaks of nano-inhomogeneities of the substrate surface and are transferred to Cl_2 molecules. After the dissociation of molecular chlorine, the quasiparticles are transferred to Cl atoms (atomic chlorine).

It should be noted that the transfer of quasiparticles occurs, only if the molecules/atoms are very close to the substrate surface ($<\lambda/2\pi$), since the optical NF is strongly localized near the peaks of nano-inhomogeneities of the surface.

The model Hamiltonian describing NF consists of two parts:

$$H_{\mathrm{NF}} = H_{\gamma-\varepsilon} + H_{\varphi-\varepsilon},$$

where $H_{\gamma-\varepsilon}$ and $H_{\varphi-\varepsilon}$ are Hamiltonians for the photon-exciton and phonon-exciton interaction systems, respectively, which have the following form:

$$H_{\gamma-\varepsilon} = \sum_p \hbar \bigg[\omega_p^\gamma \gamma_p^+ \gamma_p + \omega_p^\varepsilon \varepsilon_p^+ \varepsilon_p -$$

$$- \frac{1}{2i} \sigma^{\gamma-\varepsilon} (\gamma_p^+ \varepsilon_p - \gamma_p \varepsilon_p^+) \bigg],$$

$$H_{\varphi-\varepsilon} = \sum_p \hbar \omega_p^\varphi \varphi_p^+ \varphi_p +$$

$$+ \sum_{p,q} \big[i\hbar \sigma^{\varphi-\varepsilon}(p-q) \varepsilon_p^+ \varepsilon_q (\varphi_{p-q} + \varphi_{q-p}^+) + \mathrm{h.c.} \big],$$

where $\gamma_p^+ (\gamma_p)$, $\varepsilon_p^+ (\varepsilon_p)$, and $\varphi_p^+ (\varphi_p)$ are the creation (annihilation) operators for a photon, exciton, and renormalized phonon; ω_p^γ, ω_p^ε, and ω_p^φ are their frequencies, respectively; p and q are indices indicating the momenta of the corresponding particle (photon, exciton, or renormalized phonon) in the momentum representation; $\sigma^{\gamma-\varepsilon}$, $\sigma^{\varphi-\varepsilon}(p-q)$ are the designation of the coupling between a photon and an exciton, a phonon and an exciton; h.c. means a Hermitian conjugate.

The model Hamiltonian of NF in the exciton-polariton representation has the form

$$H_{\mathrm{NF}} \equiv H_\pi = \sum_p \hbar \omega_p^\pi \pi_p^+ \pi_p + \sum_p \hbar \omega_p^\varphi \varphi_p^+ \varphi_p +$$

$$+ \sum_{p,q} \big[i\hbar \sigma^{\pi-\varphi}(p-q) \pi_p^+ \pi_q (\varphi_{p-q} + \varphi_{q-p}^+) + \mathrm{h.c.} \big],$$

where $\pi_p^+ (\pi_p)$ and ω_p^π are the creation (annihilation) operator and the frequency for an exciton polariton; p, q are indices indicating the momenta of the exciton polariton in the momentum representation; $\sigma^{\pi-\varphi}(p-q)$ is the designation of the coupling between an exciton polariton and a phonon.

It is worth noting that electronic excitations near the nano-inhomogeneities of the substrate surface excited by the NF cause the mode-mode coupling of phonons, and they are taken into account as a renormalized phonon [8]. Therefore, multiple phonons in the form of coherently compressed phonons in the initial representation can interact simultaneously with an exciton or an exciton polariton.

The model uses exciton-phonon polaritons in the surface layers of the quartz substrate, and, therefore, their states are determined by the momentum. From the point of view of symmetry, the momentum is not a convenient quantum number for specifying the exciton-phonon polariton states at the peaks of nano-inhomogeneities. Therefore, we suppose that the quasiparticles specified by the momentum are transferred to the gaseous Cl medium.

In the mean field approximation, exciton polaritons near the peaks of nano-inhomogeneities are described

as follows:

$$\langle \pi_k \rangle = \left(\frac{I^\gamma V}{\hbar \omega^\gamma r} \right)^{1/2},$$

where I^γ is the intensity of a photon with frequency ω^γ and momentum $\hbar k$; r is the nano-inhomogeneity peak size.

Using the unitary transformation

$$\begin{pmatrix} \pi_p \\ \varphi_{p-k} \end{pmatrix} = \begin{pmatrix} i n_p^- & n_p^+ \\ n_p^+ & i n_p^- \end{pmatrix} \begin{pmatrix} \psi_p^\downarrow \\ \psi_p^\uparrow \end{pmatrix},$$

we can diagonalize the Hamiltonian in the exciton-phonon-polariton representation [9] in the following form:

$$H_{\mathrm{NF}} \equiv H_{\varepsilon - \varphi - \pi} = \sum_p \hbar \omega_p^\pi \pi_p^+ \pi_p + \sum_p \hbar \omega_p^\varphi \varphi_p^+ \varphi_p +$$

$$+ \sum_p i \hbar \left(\frac{I^\gamma V}{\hbar \omega^\gamma r} \right)^{1/2} \sigma^{\pi - \varphi} (p - k) (\pi_p^+ \varphi_{p-k} - \pi_p \varphi_{p-k}^+) =$$

$$= \sum_p \hbar \Omega(p) \psi_p^+ \psi_p,$$

where $\psi_p^+ (\psi_p)$ and $\Omega(p)$ are the creation (annihilation) operator and the frequency of the exciton-phonon polariton; $\psi_p^\uparrow$ and $\psi_p^\downarrow$ are the designation of the upper and lower branches of the exciton-phonon polariton. The transformation coefficients $n_p^\pm$ are given by the formula

$$n_p^\pm = \left(\frac{1}{2} \pm \frac{\delta}{2\sqrt{\delta^2 + 4\beta^2}} \right)^{1/2},$$

where $\delta = \omega_p^\pi - \sigma^{\pi - \varphi}(p - k)$ is the detuning between an exciton polariton and a phonon; $\beta = \left(\frac{I^\gamma V}{\hbar \omega^\gamma r} \right)^{1/2} \times \times \sigma^{\pi - \varphi}(p - k)$ is the effective coupling constant.

Thus, the Cl atom located near $(< \lambda/2\pi)$ of the peaks of nano-inhomogeneities of the surface absorbs not classical photons, but exciton-phonon polaritons, the energies of which are transferred to the atom. They excite atomic vibrations and electronic transitions that promote the interaction of atomic chlorine with the peaks of nano-inhomogeneities of the quartz substrate.

Therefore, we propose to use the exciton-phonon polariton model to describe the optical near-field interaction of atomic chlorine dipoles with the dipoles of peaks of nano-inhomogeneities of the quartz substrate in the photochemical subnano-polishing of its surface.

4. Conclusions

In the present work, the studies of the subnano-polishing of the quartz substrate surface using the optical near-field interaction of atomic chlorine dipoles with silicon dioxide dipoles are carried out.

It is proposed to use an evanescent wave for the polarization of silicon dioxide and atomic chlorine from the maximally optimal orientation of their dipole moments for the optical near-field dipole-dipole interaction using the strongest (quasielectrostatic) component of the NF $\sim 1/r^3$.

The subnano-localization of the process of photochemical etching is performed by the region of the highest near-field gradient at the peaks of nano-inhomogeneities of the surface, which attracts polarized chlorine molecules like optical tweezers.

A method for obtaining atomic chlorine by the local photodissociation of molecular chlorine using the strongest component of the optical near-field of nano-inhomogeneities of a quartz substrate is proposed.

The near-field subnano-localization of photochemical etching processes theoretically has no dimensional limitations up to the size of single atoms.

The use of the composite quasiparticle model to describe the optical near-field dipole-dipole interaction is considered.

The use of an optical NF (including an evanescent wave) allows the subnano-localization of chemical reactions. This method can be used in nanochemistry and nanotechnology.

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ДЕСТРУКЦІЯ НАНОНЕОДНОРІДНОСТЕЙ ПОВЕРХНІ
ДІЕЛЕКТРИКІВ ОПТИЧНИМ БЛИЖНІМ ПОЛЕМ

Р е з ю м е

У роботі проведені дослідження деструкції нанонеоднорі-дностей поверхні кварцової підкладки за допомогою опти-чної ближньопольової диполь-дипольної взаємодії атомар-ного хлору з SiO_2. Запропоновано спосіб отримання ато-марного хлору шляхом локальної фотодисоціації молеку-лярного хлору оптичним ближнім полем нанонеоднорідно-стей кварцової підкладки. Досліджено поляризацію атомів хлору і SiO_2 за допомогою еванесцентної хвилі, яка гене-рується на поверхні підкладки. Запропоновано метод отри-мання найбільш оптимальної орієнтації диполів атомарного хлору і SiO_2, використовуючи особливості оптичного бли-жнього поля, для максимально ефективної деструкції нано-неоднорідностей кварцової підкладки. Розглянуто викори-стання моделі складеної квазічастинки для опису оптичної ближньопольової взаємодії диполів.