

# Nano-localization of Photochemical Polishing Processes of the Dielectrics Surface Via an Optical Near Field

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## Abstract

The method of polishing a surface of a quartz substrate with a nanometer scale of roughness was investigated, using the phenomenon of optical dipole-dipole interaction of atomic chlorine with quartz. Atomic chlorine is obtained by photodissociation of molecular chlorine via an optical near field of nanoinhomogeneities of a quartz substrate. The formation of the evanescent wave on the substrate surface occurs when the substrate is irradiated at an angle of total internal reflection directed to the lower surface of the substrate. The evanescent wave polarizes the atoms of the chlorine and quartz particles, and directs them to the most effective way for photochemical sub-nano-polishing.

**Keywords:** Optical near field, Evanescent wave, Dipole-dipole interaction, Sub-nano-polishing.

## 1. Introduction

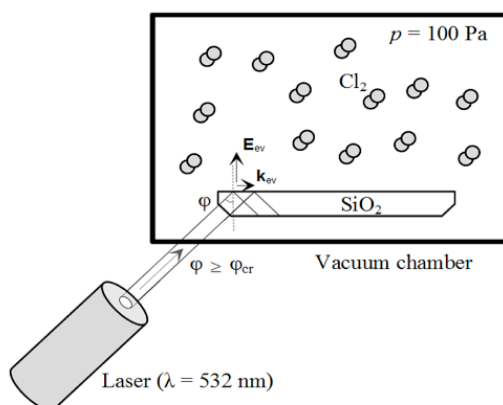
In optics, such elements as lenses, mirrors, prisms, etc., are widely used in most optical devices: microscopes, lasers, gyroscopes, and others. These optical elements are often made of quartz glass (SiO<sub>2</sub>) because of its unique properties, among which:

- wider spectral region of transparency compared to multicomponent silicate glass, especially in the ultraviolet part of the spectrum;
- the smallest refractive index among silica based glasses;
- high heat resistance and inertness to many chemical reagents.

An important feature of the aforementioned elements is the degree of homogeneity of the surface, on which the accuracy of measurements depends. Exists many ways to reduce surface roughness and, consequently, improve its quality. However, defects of the surface on a subnanometer scale can't be eliminated with usage of this methods. This can be done with usage of the optical near field [1-3], which has unique properties [4-5]. The principal difference between the near field and the classical radiation field (also called the far field) is shown in a number of studies, both theoretical [6-9] and experimental [10-12].

Quartz is a highly chemically stable material, but interacts well with atomic chlorine [1-3], which is formed by photodissociation of molecular chlorine.

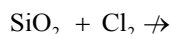
This determines the relevance of this study and the possible widespread use of the results. The purpose of the research is to develop a method for reducing the roughness of the surface of quartz substrate from tens and units of nanometers to units of angstrom.



**Fig. 1.** Experimental setup ( $\mathbf{k}_{ev}$  and  $\mathbf{E}_{ev}$  are wave vector and the electric field vector of evanescent wave respectively,  $\varphi$  is the angle of incidence of the laser radiation from the opposite side the quartz substrate surface,  $\varphi_{cr}$  is the critical angle).

## 2. Description of the study

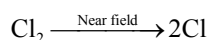
The idea of the experiment is as follows: a quartz substrate ( $\text{SiO}_2$ ) with a nanometer scale of roughness is located in a vacuum chamber (Fig. 1). The chamber is filled with molecular chlorine  $\text{Cl}_2$  to a pressure of 100 Pa. Under such conditions, the chemical activity of molecular chlorine is not enough to react with quartz [1]:

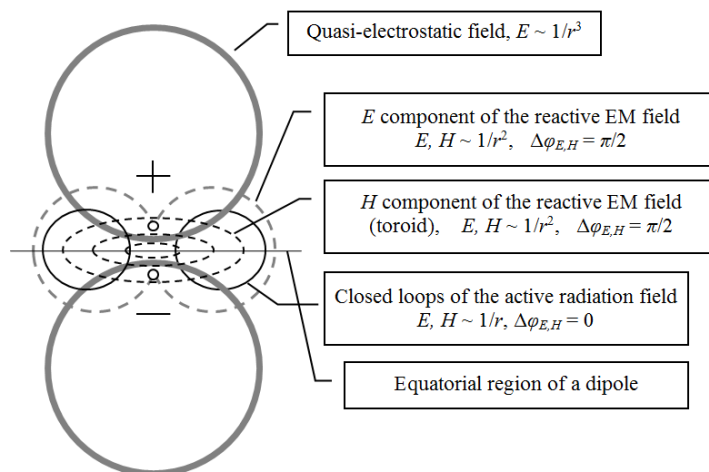


Polarization of the  $\text{Cl}_2$  molecules and  $\text{SiO}_2$  particles occurs due to interaction with the evanescent wave, which is formed at a distance  $< 85 \text{ nm}$  ( $\lambda/2\pi$ ) above the substrate surface. The formation of the evanescent wave is achieved by irradiating the substrate with a beam of green continuous wave laser ( $\lambda = 532 \text{ nm}$ ) with an energy flux density of  $300 \text{ mW/cm}^2$  below at an angle of total internal reflection. The resulting dipoles generate all three components of the electromagnetic field [13-14] (Fig. 2).

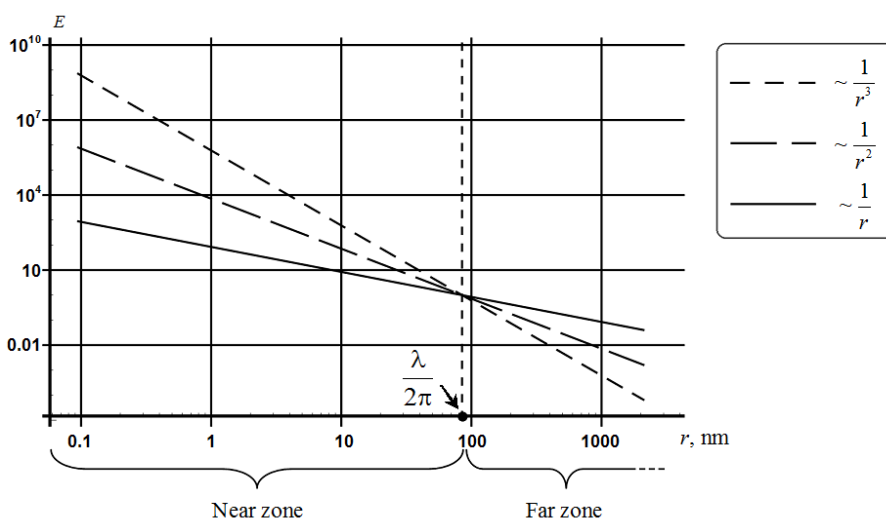
As you can see from Fig. 3, effect from the near-field component  $\sim 1/r^3$  is much stronger than the effect from reactive field  $\sim 1/r^2$  or the radiation field  $\sim 1/r$  in the near zone. The effect from the radiation field dominates only in the far zone. The Fig. 4 shows that the graph of sum of all 3 components of the electric field (marked as « $\Sigma$ ») almost coincides with the graph of  $\sim 1/r^3$  in the region I (components  $\sim 1/r^2$  and  $\sim 1/r$  are very weak). Graph of sum of components in region III almost identical with the graph of  $\sim 1/r$  (components  $\sim 1/r^2$  and  $\sim 1/r^3$  are negligible). As follows, the graph in regions I and III on a logarithmic scale should have the form of lines close to the straight lines, such as the graphs of  $\sim 1/r^3$  and  $\sim 1/r$ , respectively. All 3 components are commensurate in region II so, the graph of sum of the components in this region is a curve. Regions I, II and III are not clearly fixed.

Quasi-electrostatic component  $\sim 1/r^3$  of  $\text{SiO}_2$  leads to dissociation of molecular chlorine [1]:





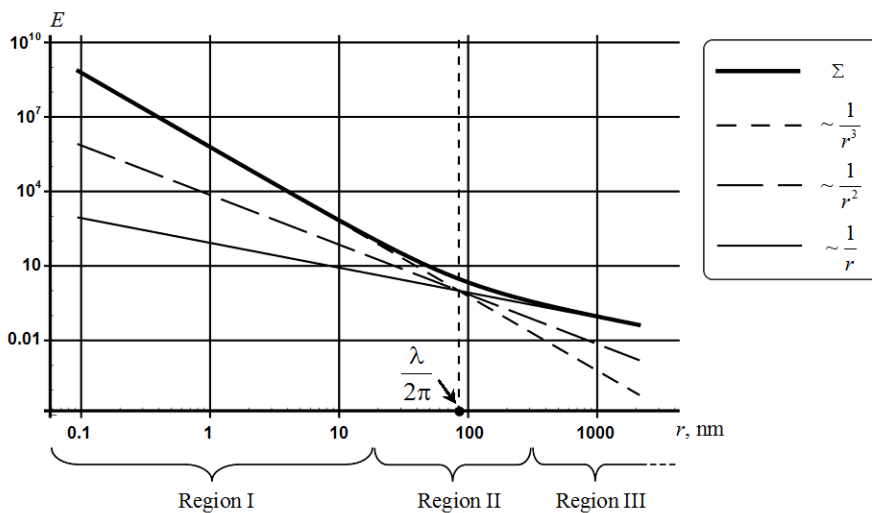
**Fig. 2.** Directional pattern of the three components ( $\sim 1/r^3$ ,  $\sim 1/r^2$ ,  $\sim 1/r$ ) of electromagnetic field generated by the dipole.



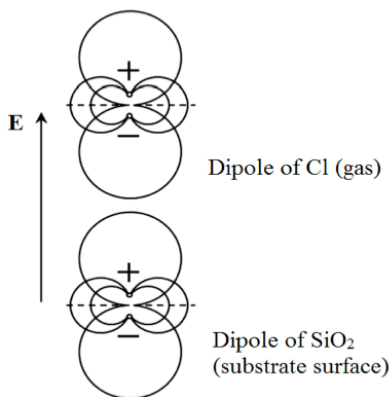
**Fig. 3.** Graphs of the dependence of the relative values of the electric field strength  $E$  on the distance  $r$  between interacting dipoles for three components of the electric field generated by the dipole.

As follows, molecular chlorine, getting into the near field, turns into more active atomic chlorine. This process is irreversible in the near field. After dissociation of molecular chlorine, atomic chlorine is polarized by the evanescent wave propagating along the surface (Fig. 1).

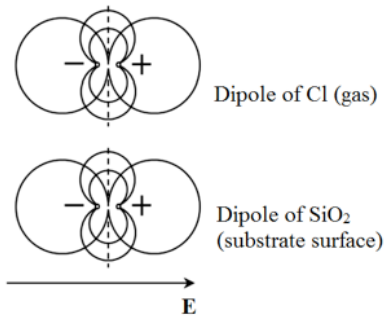
Therefore, the vector of the electric field strength of the evanescent wave is directed orthogonally to the surface plane. The dipoles (electric dipole moments) of Cl and SiO<sub>2</sub> are oriented parallel to the vector of the electric field strength. Since the near field is very inhomogeneous and decreases exponentially with distance from the substrate surface [15], it



**Fig. 4.** Graph of the relative values of the full electric field strength  $E$  (marked as « $\Sigma$ ») as a result of summing three components of the electric field generated by the dipole.



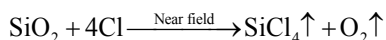
**Fig. 5.** The orientation of the dipoles of Cl and SiO<sub>2</sub> under the influence of evanescent wave when total internal reflection is used.



**Fig. 6.** The orientation of the dipoles of Cl and SiO<sub>2</sub> in the near field under irradiating the substrate from above and orthogonal to the plane of the surface.

attracts dipoles of Cl to the substrate surface. Since dipoles of Cl (gas) is always located above the dipoles of SiO<sub>2</sub> (substrate surface), then we have a situation where indicated dipoles (electric dipole moments) are oriented along one straight line and unlike poles to each other (Fig. 5). As follows, the interaction of dipoles of Cl and SiO<sub>2</sub> is due to component of  $\sim 1/r^3$ , in contrast to previous experiments photochemical sub-nano-polishing [1-3], wherein the substrate was irradiated from above and orthogonal to the plane of the surface through which the dipoles of Cl and SiO<sub>2</sub> were oriented parallel to the equatorial regions to each other (Fig. 6). With such a mutual arrangement of dipoles, their interaction was conditioned only to the component  $\sim 1/r^2$ .

Atomic chlorine reacts with nano-roughness of the quartz substrate, as the result silicon tetrachloride and oxygen, which are gases, is forming:



As a result, etching of the roughness of the quartz substrate occurs. The value of this reaction is that each particle of the nano-roughness of the quartz surface must interact with four atoms of atomic chlorine earlier than they interact with each other, which is only possible in the near field. If the laser is turned off and as follows near field is removed, then the four atoms of chlorine surrounding the quartz particle, can't react with it, primarily interact with each other and form two molecules of ordinary molecular chlorine, which does not interact with quartz. As a result, the process of photochemical sub-nano-polishing will cease.

#### 4. Conclusion

In this paper, a technique for photochemical sub-nano-polishing using an optical near field (in particular, an evanescent wave) was developed, which was allowed by the usage of the quasi-electrostatic component  $\sim 1/r^3$ . This method is more effective than methods were studied previously [1-3], which used only the reactive field  $\sim 1/r^2$ , which in the near zone has a weaker effect than a quasi-electrostatic field. As a result, the speed of the photochemical sub-nano-polishing process with usage the evanescent wave will be much higher than in previous experiments, which is an important aspect for serial production.

The nano-localization of the process of photochemical polishing is carried out in the region of the highest gradient of the near field (at the peaks of the nano-roughness of the surface), which attracts polarized chlorine molecules, like optical tweezers.

It has been shown that under the constant external pressure of the molecular gas, the optical near field allows continuous conversion of the molecular gas to the atomic gas with its subsequent local application. Thus, the use of an optical near field (including an evanescent wave) allows for the nano-localization of chemical reactions. This method can be used in nanotechnology and nanochemistry.

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## References

- [1] W. Nomura, T. Yatsui and M. Ohtsu, Nonadiabatic Near-Field Optical Polishing and Energy Transfers in Spherical Quantum Dots, in: M. Ohtsu, Progress in Nano-Electro-Optics VII, Springer, Berlin, (2010) 113–130.
- [2] G. Otsu and T. Yatsui, *Japan Patent JP2015162518A* (2015).
- [3] G. Otsu and T. Yatsui, *Japan Patent JP2016171189A* (2016).
- [4] E. Tucker, J. D'Archangel, M.B. Raschke and G. Boreman, Near-field investigation of the effect of the array edge on the resonance of loop frequency selective surface elements at mid-infrared wavelengths, *Optics Express* 23(9) (2015) 10974-10985.
- [5] A. Koshelev, K. Munechika and S. Cabrini, Hybrid photonic-plasmonic near-field probe for efficient light conversion into the nanoscale hot spot, *Optics Letter* 42(21) (2017) 4339-4342.
- [6] A.J. Yuffa, Y. Gutierrez, J.M. Sanz, R. Alcaraz de la Osa, J.M. Saiz, F. González, F. Moreno and G. Videen, Near- and far-field scattering resonance frequency shift in dielectric and perfect electric conducting cylinders, *Journal of the Optical Society of America A* 33(3) (2016) 391-395.
- [7] Y.M. Morozov and A.S. Lapchuk, Signal of microstrip scanning near-field optical microscope in far- and near-field zones, *Applied Optics* 55(13) (2016) 3468-3477.
- [8] K. Staliunas, P. Markoš and V. Kuzmiak, Scattering properties of a PT dipole, *Physical Review A* 96(4) (2017) 043852.
- [9] H.M.K. Wong, M.K. Dezfouli, S. Axelrod, S. Hughes and A.S. Helmy, Theory of hyperbolic stratified nanostructures for surface enhanced Raman scattering, *Physical Review B* 96 (2017) 205112.
- [10] D. Cao, A. Cazé, M. Calabrese, R. Pierrat, N. Bardou, S. Collin, R. Carminati, V. Krachmalnicoff and Y. De Wilde, Mapping the radiative and the apparent non-radiative local density of states in the near field of a metallic nanoantenna, *ACS Photonics* 2(2) (2015) 189-193.
- [11] R.C. Boutelle, X. Yi, D. Neuhauser and S. Weiss, SOFI for Plasmonics: Extracting Near-field Intensity in the Far-Field at High Density, *ACS Nano* 10(8) (2016) 7955-7962.
- [12] E. Tucker, J. D'Archangel and G. Boreman, Near- and far-field investigation of dark and bright higher order resonances in square loop elements at mid-infrared wavelengths, *Optics Express* 25(5) (2017) 5594-5608.
- [13] V.S. Sydorenko, Y.O. Gayday and S.V. Zhyla, Peculiarities of the near-field of a Hertz dipole, *Bullet. Univ. Kiev. Ser.: Phys. & Math.* 2 (2005) 365-372.
- [14] V.V. Nikolskiy, *Electrodynamics and propagation of radio waves*, Nauka, Moscow, 1973.
- [15] V.M. Ogenko, V.M. Rozenbaum and A.A. Chuyko, *The theory of oscillations and reorientations of surface groups of atoms*, Naukova dumka, Kyiv, 1991.