Solid-state photochemistry as grounds of photolithography technologies

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The brief review is devoted to the explosively-developing branch of the chemistry – the solid-state photochemistry. It contains three main parts: the photochemistry in the crystalline state, the photochemistry in the polymer and glass-like matrices, the solid-state photochemistry as a basis for photolithography science.
*Keywords: solid-state photochemistry, topological principle, crystalline packing, reaction cavity, free volume, hydrogen bond, photosensitive inhibitors of the polymer dissolution.*

1. Introduction

Photochemical reactions in the solid states are important for many areas of modern chemical science and technology. Transfer of the reactions from the gaseous or liquid phase (where there has place high degree of reagent mobilities) into the solid phase leads not only to retarding of chemical reactions due to reduction of probability of the reactants fragments meeting that is necessary to realize of the reaction but also significantly increases reaction selectivity due to "good" molecular arrangement of reagents for the "target" way of the reaction. Because of this, it is possible to control of the chemical reaction processing [1-6]. A new direction - supramolecular chemistry – has appeared in modern chemistry [7,8]. Typically, the molecules in the supramolecular systems are bonded by intermolecular interactions. The supramolecular chemistry has come from the solid-state chemistry originally developed for the reactions in the crystalline state.

Photolithography is one of the most important method of the micro- and nanoelectronics technologies to produce elements of integrated circuits and other electronic devices having micro and sub-micro dimensions [9,10]. The photolithography flowchart is shown in Fig. 1.

The photolithography process consists usually of the following obligatory steps. The photosensitive composition (named photoresist) deposited onto a substrate (being a foundation of an integrated circuit) by means of spin-coating and drying process, gas plasma deposition etc. The formed coating is baked to avoid its out-gassing and to enhance adhesion of a photoresist layer to the substrate.
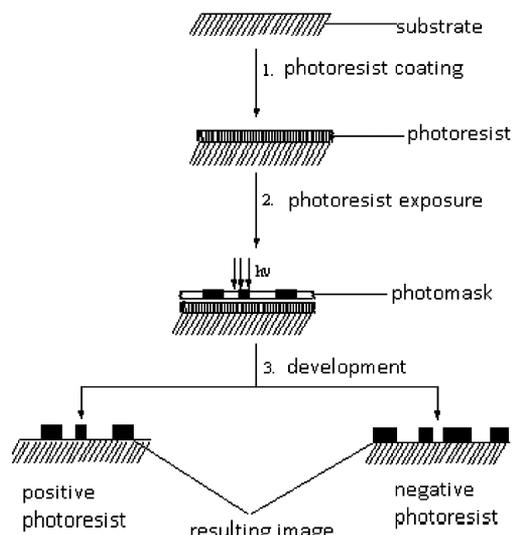
Fig. 1. The flowchart scheme of the photolithography process

Next step of the photolithography process is ultra violet or electron beam irradiation that changes the irradiated part properties of the photoresist film. The corresponding reaction initiates changing of the solid photoresist (usually changing its solubility). If the solubility of the irradiated parts becomes higher than the photoresist is named as a positive photoresist otherwise it is a negative photoresist. The next stage named a development uses the obtained difference in the physical properties of the irradiated parts of the photoresist to produce so called a photoresist mask that could be used for

etching of the substrate, implantation of ions into it, deposition of special layers and so on.

It is important to point out that during or after exposure of the photoresist under ultra violet or electron irradiation there have place photo- or radiation induced chemical reactions in the solid state. If we could found out the way to control the reactions (their effectiveness and selectivity), we could obtain the keys to control the photoresist functionality.
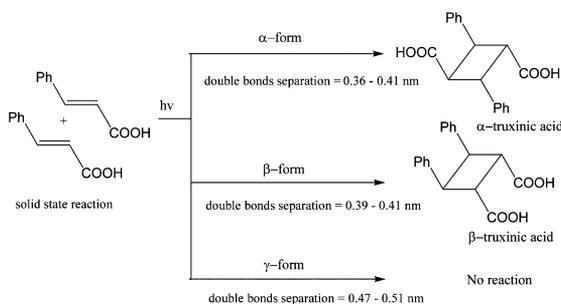
Unfortunately, the investigations of the photoresist selection and improvement of its properties based upon the solid-state reactivity consideration are quite rare. To review them and to draw the trends of their developments is aim of the paper.

2. Solid state reactivity of the organic photosensitive compounds in the crystalline state

The solid-state photochemistry has appeared after the fundamental works by Schmidt et al [11-16] where it was demonstrated a strong relation between solid state structure of reagents and their photochemical reactivity. Later on, this direction of research has become into explosively developing part of the chemistry [17-25]. Unfortunately, the Schmidt approach is usually applicable only for crystalline or polycrystalline substances. Some work has been done to suite them to non-crystalline substances where there is no strict ordering being characteristic for the state [26-34].

So, supramolecular structural transformation in crystals triggered by physical stimuli such as light, heat and small molecules is an emerging field in crystal engineering [32]. The classical example of the photochemical topotaxy is shown in Fig. 2. Schmidt and his coworkers [14] emerged the important set of topochemical rules connecting the configuration of the product and the crystal structure of the starting cinnamic acids.

The important results obtained by analyzing the solid-state behavior of these compounds are the following:

(1) The product formed is governed by the environment rather than by the intrinsic reactivity of the reactive bonds in the crystalline state;

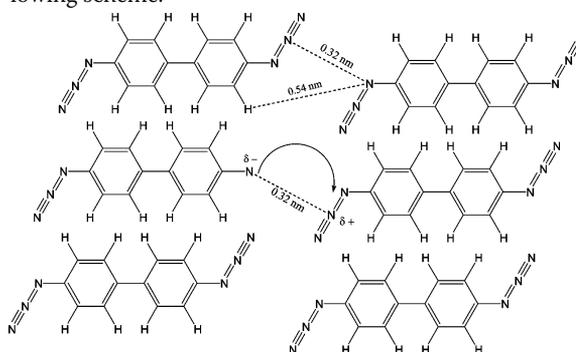(2) The proximity and degree of parallelism of the reacting centers are crucial for the dimerization;

(3) There is a one-to-one relationship between the configuration and symmetry of the product and the starting reagents.

Zelentsov et al [21] presented further illustration of the important role of the topotaxy principles in the solid-state reactions of organic diazides under UV and electron beam exposure. Fig. 3 illustrates the crystal structure of the 4,4'-diazidodiphenyl obtained by molecular mechanics [21].
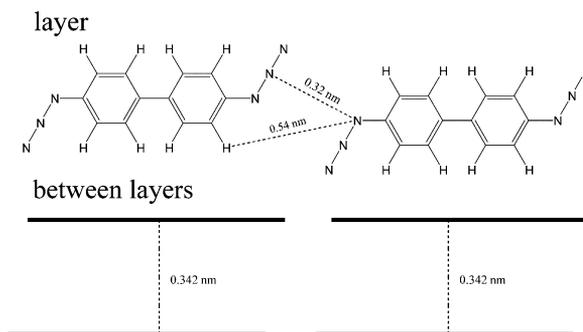
Fig.3. The crystal structure of 4,4'- diazidodiphenyl obtained from molecular mechanics calculations [21].

Opposite to the solution chemistry, this azide forms azopolymer in the photopolymer reaction occurring in the crystalline state [21]. The electron density transfer from the nitreneous nitrogen atom to the middle nitrogen atom of the azide group of the adjacent azide molecule plays a central role in the mechanism. The layered crystal structure of the azide and suitable juxtaposition of the adjacent molecules favor the reaction way shown in the following scheme.


It is important to note that other azides studied (such as 4,4'-diazidodiphenyl ether,

Fig.2. Photochemical transformation of cinnamic acids in the crystalline state (from [14])

2,6-di(4'-azidobenzylidene)-4-methylcyclohexanone, 4,4'-diazidobenzophenone *etc.*) have not had a possibility to adopt the crystal structure similar to the crystal structure of 4,4'-diazidodiphenyl and the yields of azopolymer in the latter case were greatly lower.

The topological principle has been constantly attacked and modified [27, 35]. The main idea of the modifications was an attempt to include into consideration rotational, twisting and translational motions. Kaupp has shown [35] that application of AFM to the solid-state photopolymerizations revealed previously unexpected long-range molecular movements in the initial stages (phase rebuilding) and in the stages (phase transformation and disintegration) of the reaction. He has stated that the most of the solid-state reactions proceeds in such a way that the crystals are disintegrated and the space groups of the product crystallites are different from that of the starting molecules. Unfortunately, Kaupp and his followers do understand the topological principle too strictly. It seems that Schmidt et al have noticed that minimal atomic and molecular movements in the solid-state reactions and the limiting distances between atoms take an active role in the solid-state processes only in the starting molecular system. They should be applicable only to part of the reaction path from the starting to the intermediate stage of the solid-state process with obligatory inclusion of possible long-term movements to move reaction sites of the reagents closer at the later parts of the path. After that moment the reaction follows the Schmidt principle again. Kaupp is certainly quite right to state that molecular movements sometimes show to be very long term because the product molecules with different shapes do not always fit in the starting lattice. In addition, we should to consider not the only reaction path but a set of ways realizing with different probabilities. The probabilities could differ greatly not only for different reactions but sometimes they could vary in the course of the reaction.

Thus, the Schmidt principle should be consider not apart from the molecular and atom movements but together with them. Photoreactive olefinic double bonds have been successfully aligned to satisfy the Schmidt geometric criteria for photoreactivity in the solid state *via* reagent staking, hydrogen bonding, halogen bonding, coordination bonding, both hydrogen and coordination bonding in discrete and infinite molecular assemblies. The topochemical approach requires minimal atomic and molecular movements in the solid-state reactions. However, quantitative yield of products in several solid-state reactions, including [2+2] photocycloadditions, cannot be explained exclusively on the to-

(a) (b)
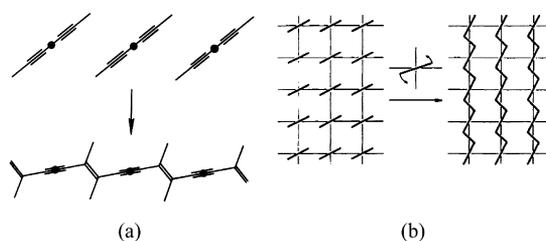
Fig. 4. Hirshfeld - Schmidt model of polymerization of compounds such as diacetylene dicarboxylic acid. The solid-state process is diffusionless, and rotation of the monomers enables them to link up with their neighbors without any change in linear separation of the repeat units upon polymerization: (a) diacetylene dicarboxylic acid [12]; (b) general scheme [36].
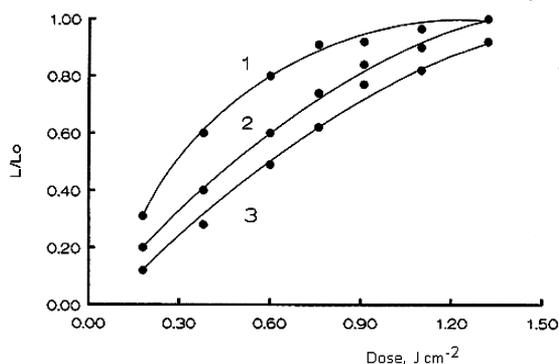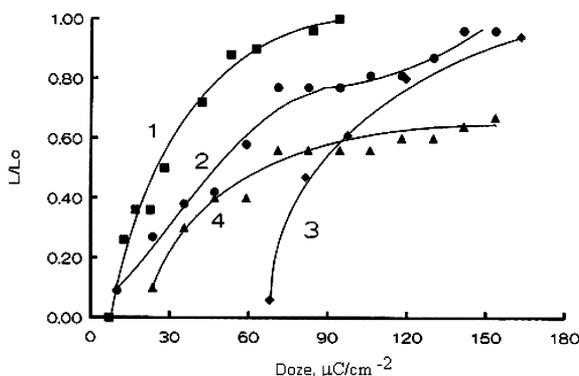

Fig. 5. Characteristic curves of diazides layers in the case of UV exposure:
1 – 4,4'-diazidodiphenyl; 2 – 4,4'-diazidodiphenyl ether ; 3 – 4,4'- diazidobenzophenone

pochemical postulate base. Sometimes, such reactions require large molecular or atomic motions in the solid-state lattice. External forces such as light irradiation or mechanical motion induce molecular motion in the crystal lattice. Large pedal-like motions of double bonds in solids prior to dimerization were observed [28-30]. Some typical movements leading to the solid-state reactions are shown in Fig. 4.

Zelentsov et al [21] have tried to use topochemical principle to choice aromatic azides for the dry photolithography. Fig. 5 and 6 contain characteristic curves for exposure of some azides in the crystalline state.

The inspection of the curves and the azide packing (Fig.3) give an opportunity to jump to conclusion that 4,4' – diazidodiphenyl has the highest sensitivity for high energy exposure and is the most suitable azide to be used as photo- or electron-beam resist in dry lithography processes.

Fig. 6 Characteristic curve of diazides in the case of E-beam exposure: 1 – 4,4'- diazidodiphenyl; 2 – 4,4'-diazidodiphenyl ether ; 3 – 4,4'- diazido-benzophenone; 4 – 4,4'- diazidobenzalacetone

It is important to note that presence of large void volume or empty channel in loosely packed crystals with weak hydrogen bonds are able to stimulate molecular movements in solid state. The molecules are able to migrate easily if they are not interlocked inside the crystal packing.

3. The solid-state reactivity in polymers or glass-like systems

The most important role in governing of the solid-state reactivity plays free volume of the polymer or glass-like matrix. One of the first who used the free volume concept to describe properties of condensed systems was Franc [37, 38]. According to his theories, in a system of atoms whose motions are classically excited, the change in entropy in any isothermal process can be written as $R \ln \left(\frac{v_{f2}}{v_{f1}}\right)$ per mole, one such term for each kind of atom in the system. The term v_f used is the effective volume accessible to the center of gravity of the atoms. Corresponding expression can be written for the classical (translational and rotations) part of the motions of polyatomic molecules in the real liquids and solids. In the solids, the free volume can be written as $v_f = N \cdot v \cdot f$ where v is a box or cage, volume accessible to one of articles, and f, the fluctuation factor, which depends on the way in which the box is defined. $R \cdot \ln f$ is a contribution to the entropy of system («fluctuation entropy»). The fluctuation entropy induces «communal entropy» as well as term due to the temperature variability of cell sizes. The free volume of a momoatomic crystal can be determined as

$$P_{vap} = \frac{RT}{v_f} \cdot exp\left(-\frac{\Delta H}{RT}\right)$$

This equation gives the method to calculate free volume from the evaporation characteristics.

In addition, a good additive scheme to estimate free volume of polymer as a sum of the func-

tional group contributions was proposed by Ascadskii [39,40] .

The main tools to investigate the chemical reaction in the system with high reagents mobilities are the electronic theory, the transition state concept, and the concept of solvation. The tools give the opportunity to provide adequate means to describe chemical reactions and to predict their results. The impact factors in the batch chemistry are essentially connected with electronic effects or being their secondary effects. There are no surface effects (if the reaction is in the kinetic regime) and the solvent effects bases greatly upon the solvation concept proposed by Hughes and Ingold [41].

In the case of chemistry with restricted reagent mobilities the situation changes dramatically. The surface effects, the specific viscosity influence, the reaction cavity concept, the impact factors inducing specific orientations of the reactants, free volume concept, etc. become dominant. There is a certain gap between theoretical concepts and approaches being useful in the high and restricted reagent mobility sistems should be different.

The transition state theory in its classical version is not completely suitable to be used in the systems with low reaction mobility. Is it could be used in the solid-state chemistry?

To study a reaction path it is profitable to consider the elementary events in the reaction as independent ones. Then the probability of the reaction path is a product of the probabilities of the elementary events composing the reaction path. In other words, for the reaction $A \rightarrow B$ there would has place a relation

$$p(A \rightarrow B) = \prod_{i=1} p(C_i)$$

Here $p(A \rightarrow B)$ is a probability of the transformation of A to B, C_i, i =1, 2, …, is a set of independent events forming the complete system under consideration, and $p(C_i)$ is a probability of the C_i event.

Kramers [42] seems to be the first who presented a reaction rate constant as a product of two multipliers: the first one related with so called friction of the molecules in the reaction media, the second one is the usual Arrhenius' exponent related with activation energy. He derived a relation for reaction rate constant k_R for a reaction having place in a solvent with moderate-to-strong friction

$$k_R = \frac{1}{\omega_b} \cdot \left(-\frac{\gamma}{2} + \sqrt{\frac{\gamma^2}{4} + \omega_b^2}\right) \cdot \frac{\omega_R}{2\pi} \cdot exp\left(-\frac{E_b}{k_B T}\right)$$

where γ is friction constant related to diffusion coefficient by Einstein's relation, $\gamma = \frac{k_B T}{D}$, ω_R and ω_b are the frequencies that confine the parabolic reac-

tant well and barrier top respectively, E_b is an activation energy, T is temperature, k_B is Boltzman constant, and D is diffusion coefficient. From that formula one could deduce that the transition state theory gives the upper estimate for the true reaction rate constant [63]. The second consequence of the relation found that the joint probability could really be presented as a product of probabilities of the chemical events leading to the reaction in the systems with low reactants mobility.

It seems to be useful to discuss some of the typical reaction events C_i for the first order reaction.

Event C_1 is the $A \rightarrow B$ chemical transformation in vacuum or in solvents of low viscosity and low reactants concentrations. The reaction could be described by means of the standard transition state theory being the real basis to forecast reactivity. Probability of the event could be determined from the well-known formula

$$p(C_1) = F \cdot exp\left(-\frac{E_b}{k_B T}\right)$$

Here F is so called pre-exponential factor, E_b is activation energy of the $A \rightarrow B$ transformation obtained, for example, experimentally or from quantum chemical calculation of the transition state and initial reagents enthalpies with the zero point energies inclusion, k_B is Boltzmann constant, and T is temperature (in K).

The transition state theory should be a central cornerstone in reaction dynamics having place in the condensed media [43, 44]. The key step of its implementation is the identification of a dividing surface that is crossed only once by all reactive trajectories. This assumption is often badly violated especially when the reactive system is coupled to an environment [44], so the calculations made in vacuum usually overestimate the reaction rate.

C_2 is an event when there is no enough free volume in the reacting system for the chemical reaction to occur successfully with the certainty. The value of free volume should be enough for formation of the transition state configuration in the reaction system.

Batchinski seems to be the first who stated out that viscosity of liquid could be described as a function of "relative volume of molecules per unit of free space" [45]. The idea was widely used by Frenkel in his theory of the fluidic state [46]. Doolittle [47] found a good empirical relation

$$\eta = A \cdot exp\left(\frac{B \cdot v_0}{\Delta v}\right)$$

Where $\frac{\Delta v}{v_0}$ is the ratio of extra volume the liquid molecules occupy at the real temperature because of thermal expansion to the volume of liquid extrap-

olated to 0 K, A and B characterize the substance used. Cohen and Turnbull [48] explained this relation by modeling liquid molecules as a collection of hard spheres. Free volume was defined as the volume in excess compared to an ideal atomic configuration at the maximum density [49]. The extra volume is generated between the molecules moving around due to thermal fluctuations.

There were many efforts to find correlation between free volume, reagent volume and reactivity of it in dense matrices. Sometimes they were successful [50-59]. For instance, Zelentsov et al [51] have found that ratio of rate constants of oxidation reactions of nitrene in the polymer matrices could have a form of $exp\left(-\alpha \cdot \frac{V-V_{ref}}{v_f^0}\right)$, where α is a constant, $V-V_{ref}$ is change in the reagent volumes from the reference to the studied reagent and V_f^0 is the free volume in the polymer matrix per its monomer unit. Fig. 7 illustrates the dependence of the relative concentration of the azide photooxidation products formed in the cyclized resin matrix on the nitrene volumes [51].
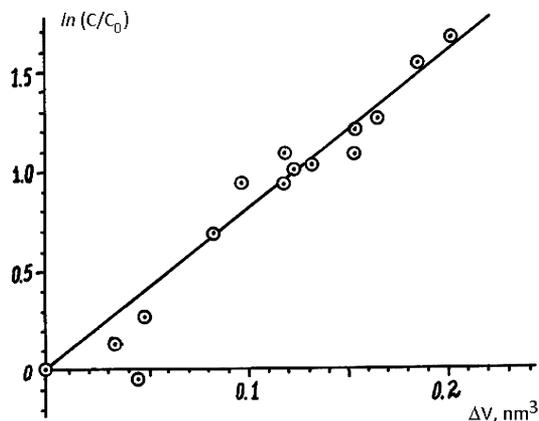
Fig. 7 The dependence of the relative concentration of the azide photooxidation products formed in the cyclized resin matrix on the nitrene volumes [51].

The authors observed [51] that the ratio of the relative rates in different polymer matrices is proportional to a quantity of

$$V \cdot \left(\frac{1}{V_f} - \frac{1}{V_f^{ref}}\right)$$

where V_f and V_f^{ref} were related to the studied and reference matrix. Taking the relation into account one could propose the following expression for the probability of the turning of the initial state of the reaction system into its transition state

$$p(C_2) = F \cdot exp\left(-\alpha \cdot \frac{\Delta v_R}{v_f^0}\right)$$

where $\Delta v_R = v^{\neq} - v_R$, $v^{\neq}$ and V_R are volumes of the molecule in the transition state and in the initial state of reagents.

The useful complementation of the free volume concept seems to be a concept of «reaction cavity» [60-62] as a region of space in which the reactive system is located. In that case the free volume concept could explain not only chemical reactivity but the selectivity of the reaction. For example, the selectivity of photochemical rearrangements of 1-naphthyl and 2-naphthyl acylates has been investigated in polyethylene [59]. The *ortho*-positronium accessible free volume sites in the undoped polyethylenes have been measured by positron annihilation lifetime spectroscopy. These void free volumes are much smaller than the van der Waals volumes of the naphthyl molecules under investigation. The naphthyl esters inside polyethylene cavities act as templates for the formation of their photoproducts. Long alkyl chains on naphthyl myristates not only affect the shape anisotropy but also induce large van der Waals interactions with the walls of reaction cavities. Stretching enhances the templating effect and strengthens the van der Waals attractions with cavity walls in the case of naphthyl myristates, thus inducing marked increases in reaction selectivity in polyethylene films.

C_3 is an event when the free volume is localized nearby the transition state so as it is desirable for the reaction to progress successfully. The concept of the proper localization of free volume appeared in many works such as [63-66]. One can build free volume maps showing the free volume distribution in the reactive cavity and serving useful tools to forecast possible reactivity in the system with low mobility of reagents. To obtain the proper) expression for $p(C_3)$ one needs to know detailed mechanism of the reaction and have some information on the mutual disposition of the reactive molecules and reaction cavity structural entities. Probability $p(C_3)$ should be equal to 1.0 if the reagents and transition state could be represented as spherical entities, it should be of the form

$$p(C_3) = \Phi \cdot exp\left(-\frac{\Delta\varphi}{\varphi_0}\right)$$

where Φ and φ_0 are constants and $\Delta\varphi$ is an angle between directors of the free volume cavity and the reactant molecule if the reagent(s) and transition state could be represented as ovals or tubes etc.

In addition to the phenomena described there exist ones concerning of the peculiarities of flows in the reaction system with low mobilities oh reagents. Holyst et al have investigated the unusual behavior of viscosity in systems with various dimensions of solute and solvent [67]. It turned out [67,68] that objects several billion times smaller than macro-

scopic objects can "feel" viscosity several hundred and even thousand lower than a macroscopic object. Hołyst et al have shown that in each reaction system there is a fundamental length scale when a transition from macro- to nanoviscosity occurs. The size of this scale depends on the size of objects present in the reaction system: in the case of polymers it will be the size of a random coil. An object larger than the coil immersed in the polymer solution feels macroviscosity and smaller one feels nanoviscosity. Holyst et al [69] measured the viscosity of poly(ethylene glycol) (PEG) in water with nanoscopic probes of different diameters (from 1.7 to 114 nm). For a probe of diameter smaller than the radius of gyration (R_g) of PEG the measured nanoviscosity was of orders of magnitude smaller than the macroviscosity. For the probes with sizes equal to or larger than the polymer R_g macroscopic value of viscosity was measured. A relation for macro and nanoviscosity was found to be a function of R_g for PEG, correlation length in semi-dilute solution, ξ, and probe size, R. For $R < R_g$, the nanoviscosity (normalized by water viscosity) is given by $exp(b(R/\xi)^a)$, and for $R > R_g$, both nano- and macroviscosity follow the same curve, $exp(b(R_g/\xi)^a)$, where a and b are two constants close to unity. Such strong dependence of viscosity on the sizes of solute and solvent used should have a tremendous effect on the reactivity in the systems with low mobilities of reagents.

Murugan et al. [70, 71] found out that there had place some orientational ordering in the solid state under pressure.

There of course exist other contributions, $p(C_j)$, into the joint probability of the reaction realization. Next researching will certainly light them on.

Weiss and his coworker [72] have develop the free volume concept. They noted that central to the complexity of describing the reaction sites in the isotropic media is the initial special distribution and temporal redistribution of free volume which must be present at a site in sufficient quantity if reactant molecules are to be able to undergo the shape changes required for their transformation to products.

Weiss et al [72] have modified a concept of "the reaction cavity" originally developed by Cohen to describe reactions in crystals [73]. Weiss has postulated that cavities may be separated into three categories: an "initial reaction cavity" (defined by the space in which the excited states of reacting molecules are generated), a "total reaction cavity" (which encompasses the space and molecular environment which the excited molecules and their intermediate explore from the time of their inception to the movement of their final product determining steps), and "final reaction cavity" (which includes only the sites in which the product determining steps occur).

Very promising part of the free volume concept seems to be stiffness or hardness of the cavity walls [72]. The crystalline materials, interplaner regions of clay, and interior of zeolites possess time dependent structures in which free volume is essentially stationary and constant. The free volume needed to accommodate shape changes which occur during the course of these reactions must be intrinsic to the host since the walls of the cavities are stiff or hard. In the case of solid poltmer matrices, micelles, molecular aggregates, liquid crystals and so on free volume can migrate and vary locally with time, so that an initial cavity may include inadequate free volume for reaction to proceed but acquire it subsequently. In that case the walls of such reaction cavity can be considered as flexible or soft.

Weiss et al [72] have also introduce a concept of coincidence between the form of the reaction cavity and the form of the reactants involved in the reaction. The idea was illustrated by Fig. 8 [72].
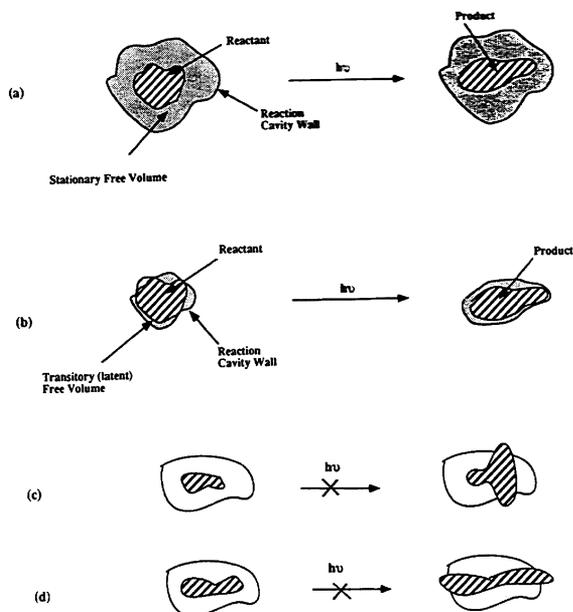
Fig. 8. Different cases of the reaction cavity and reactants forms coincidence [72].

Here, there have place three main situations. In the case (a) the volume of cavity prevails the sum volume of the reactants and the reaction does not depend on both the form and stiffness of the reaction cavity and the form of reactions. In the case (b) the reaction cavity and the reactants are almost coincident, and the reaction probability is greatly dependent on the cavity walls stiffness, it will be retarded if the stiffness is too large. In cases (c) and (d) the reaction cavity form and the reactants form

differ too strong to give an opportunity for the reaction to proceed successfully.

4. Solid state kinetics

The kinetics of the solid-state reactions greatly differs from the kinetics in the liquid and gaseous phase. The problem is quite difficult if one considers that within the lattice molecule do not have an equal probability of undergoing a chemical reaction [74].

A simple and general method for the analysis of this type of kinetics was proposed by Avrami and Erofeev[75, 76] and had a form of

$$[- ln (1-\alpha)]^{1/n} = k \cdot t$$

where α is completion of the reaction, k is reaction constant, n is a constant related with nucleation, t is time.

A similar approach has been proposed by Sharp and Hancock [77]

$$ln[- ln (1-\alpha)] = n \cdot ln t + b.$$

Here n and b are constants.

The equation is clear enough in the range $0.15 < \alpha < 0.5$. There are some choices of n value [78]. If $n \approx 0.5$ then there has place a diffusion-controlled mechanisms; for $n = 1$ a phase-boundary control is appropriated; $n = 1-2$, $n = 2-3$, and $n = 3-4$ are consistant with nucleation and growth via a one-dimentional, two-dimentional, and three-dimentional growth, respectfully. These simple but useful equations were successfully used for great amount of reactions.

Further development of these model can be find in some works [79-85].

The real grounds for description of the solid state kinetics are only appearing. Their creation will be a real triumph in the solid-state science.

5. Supramolecular photochemistry as the real ground for the development of new photolithography methods

Physical and chemical mechanisms of photolithography have not been studied extensively. There are a small number of fragmentary works devoted to this problem.

The main disadvantage of the known mechanisms is insufficient taking into account of the reactants limited mobility and the presence of nonvalent bonds between the polymer matrix and the photosensitive substance. The proposed project seeks to address these shortcomings.

It was previously excepted [9, 86,87] that the basis of photochemical reactions of *ortho*-naphthoquinonediazide (NQD) compounds being responsible for the formation of relief images is their

photochemical decomposition to carbenes and molecular nitrogen, rearrangement of carbenes into ketenes, the conversion of ketene in indene carboxylic acid in the presence of residual amount of water in the polymer. However, there are several experimental and theoretical results that not fit into the above scheme [88-90].

It has been suggested that a change in solubility of the systems containing NQD compound and novolac resin after the UV light irradiation is responsible for a change of intermolecular hydrogen bonds between the photosensitive component molecules and macromolecules of novolac resin [88, 89, 91, 92]. Previously proposed mechanism should be supplemented by the following hypothesis: decomposition of NQD derivative leads not only to the hydrophilic indene carboxylic acid, but also to destruction of the hydrogen bonds between the NQD derivative and macromolecules of novolac resin. In addition, nitrogen gas produced in the course of the reaction forms microchannels in bulk photoresist. All mechanisms mentioned contribute to the penetration of water molecules into exposed areas of the photoresist. This change of solubility of the photoresist being responsible for the formation of a positive relief in systems consisting of NQD moieties and novolac resins.

Thus, although the hypothesis of the decisive role of density and strength of intermolecular hydrogen bonds between the photosensitive material molecules and novolak resin and have been offered before but detailed physical and chemical mechanisms of this influence have almost not been studied.

Previously, it has been shown an opportunity of a successful theoretical study of the properties of hydrogen bonds and their role in the acidolysis using methods of molecular dynamics and modern quantum chemistry [93-98].

FTIR spectroscopy investigations were previously limited by studying of the physical and chemical processes in the systems of the hydroxyl-containing polymers and derivatives of NQD derivatives [99-103], but such researches have not received broad implementation.

Unfortunately, in a great majority of available works there no has place a physico-chemical explanation of processes occurring in photoresist. This leads to poorly controlled processes of photolithography and to difficulties of the process parameters optimization.

Another objective is to change the development of methods to eliminate deterioration of the functional properties of photoresists during storage. It is worth to note that this problem was successfully solved by addition of hydrogen-bond forming substances to the photoresist composition.

Finally, it can be assumed that increasing of plasma resistance of the photoresist film can be achieved by increasing the density of the crosslinking and/or non-valent interactions. The study of literature has shown that the increase in the degree of crosslinking does increase plasma resistance of photoresists [104], obviously due to free volume decrease. However, it is necessary to study the degree of crosslinking of the photoresist, and the results of calculation of geometrical parameters of the structure of the photoresist mask to get unambiguous understanding of the mechanism of the plasma resistance increasing.

5. Conclusion and outlook

Last three decades were periods of extensive development of the solid-state chemistry and its transformation into important branch of modern chemistry and technology. The most striking feature of it is at the unique opportunity to control chemical reaction mechanisms and chemical reactivity *via* special building up (engineering) of the chemical reaction system structure. Due to the restricted mobilities of the reagents, a chemist receives the unique opportunity to combine in one synthesis high efficiency and selectivity of the chemical process. The ability to build up special reaction system structure that facilitates a movements of the reaction system to the transition state and to the final products structure. Besides, the restricted mobility gives rise to strict choice of possible reaction ways.

There exist very powerful simulation methods such as molecular mechanics, dynamics, and Monte Carlo techniques that give possibilities to predict structural peculiarities of the solid-state system. The method can be combined with quantum chemical and spectroscopy researches to produce more fruitful scientific approach.

Nowadays, we can state that the solid-state chemistry has gains the real grounds for lithography being one of the most important methodology of the modern micro- and nanoelectronics.

It should be foreseen a great further development of the solid-state chemistry. One could name some branches of the process: (1) there will be tremendous implementation of the solid state methodology in organic and inorganic syntheses; (2) the solid-state chemistry could be combined with micro- and nanoreactor technologies (both direction have almost the same goals); (3) method of computational simulations of the solid state systems will receive its development; (4) there will be tremendous development of the solid-state photochemistry; (5) the control of chemical reactivity will be the most striking feature of chemistry in the nearest future.

The modern lithography needs new processes, novel substances, ideas. The solid-state chemistry concept should be a real ground to meet powerful impulses of the electronics development.

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