

## CONTROL OF THE RATE OF THE INTERFACE ADVANCE IN TOPOCHEMICAL REACTIONS

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The reaction of thermal decomposition of copper hypophosphite at temperatures above 50 °C involving the formation of metallic copper particles proceeds by the way of formation and growth of nuclei—the sites of the transformation. The rate of nuclei formation is determined by the presence of defects of a definite type in the crystal. The primary course of the reaction at the reactant–nucleus interface is determined by permeation into the unreacted regions of the active intermediate decomposition product—hypophosphorus acid. Methods of controlling the acid diffusion and the rate of the interface advance are proposed.

The use of the thermal decomposition reaction of a copper hypophosphite layer for metallization of the surface of a dielectric is discussed as an example of applying the control of the interface advance rate for serving the purposes of technology.

**Key Words :** Interface; Topochemical Reactions; Copper Hypophosphite; Thermal Decomposition; Product Nuclei; Metallization

AN important problem of topochemistry of thermal decomposition is that of controlling two basic topochemical parameters: the formation rate and the growth rate of the product nuclei.

A scheme of a topochemical decomposition is given in Fig. 1. The nuclei of the product are formed and they grow. Depending on the relation between the rate of nuclei formation and that of nuclei growth the decomposition can proceed in different ways, for example, in the way as shown in Fig. 1*b*, or through formation or growth of one nucleus.

If a topochemical decomposition is conducted for technology purposes, the way of the decomposition determines the properties of the product and success of the process. If the single crystal or polycrystalline layer in Fig. 1 decomposed for the production of a metallic electroconducting product, the electric resistance between the A and B electrodes depends on the way of the decomposition. In many technologies is of importance the possibility of controlling the basic topochemical parameters.

What is the state of the theory and practice of control of these parameters?

There is a developed theory of controlling the rate of nuclei formation.<sup>1</sup> Its basics are as follows :

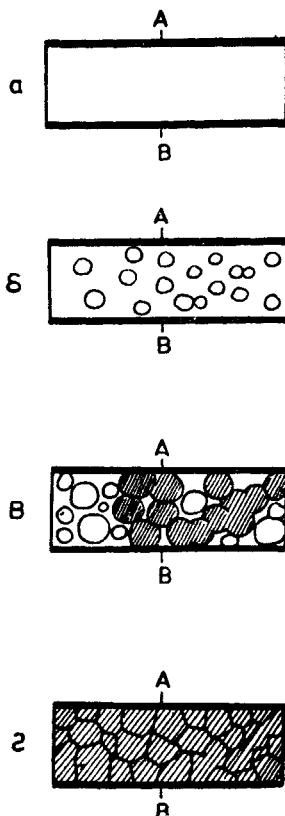


FIG 1 Schematic representation of topochemical decomposition of a crystal region or layer between electrodes *A* and *B*. The decomposition time increases in succession from *a* to *d*. The electroconducting part is section-lined.

A topochemical reaction starts at the defect sites of the crystal at which the formation of nuclei is facilitated. To determine which kind of defects necessary this one should study the mechanism of the early stages of the reaction, and then introduce the necessary defects into solid.

Consider now how this theory works in the case of a particular substance—solid copper hypophosphite  $\text{Cu}(\text{H}_2\text{PO}_2)_2$ .

Fig. 2 shows a mechanism of the thermal decomposition of copper hypophosphite. The initial stage of the reaction is the formation in the solid of an active molecule of hypophosphorus acid containing a three-coordinated phosphorus. A hypophosphite ion in the active form and a labile proton are necessary for this. By changing the concentration of these defects it is possible to change the rate of nuclei formation and, correspondingly, the time of induction period of the decomposition.

Fig. 3 gives kinetic curves of the thermal decomposition of copper hypophosphite: of both the pure substance containing thermodynamically equilibrium

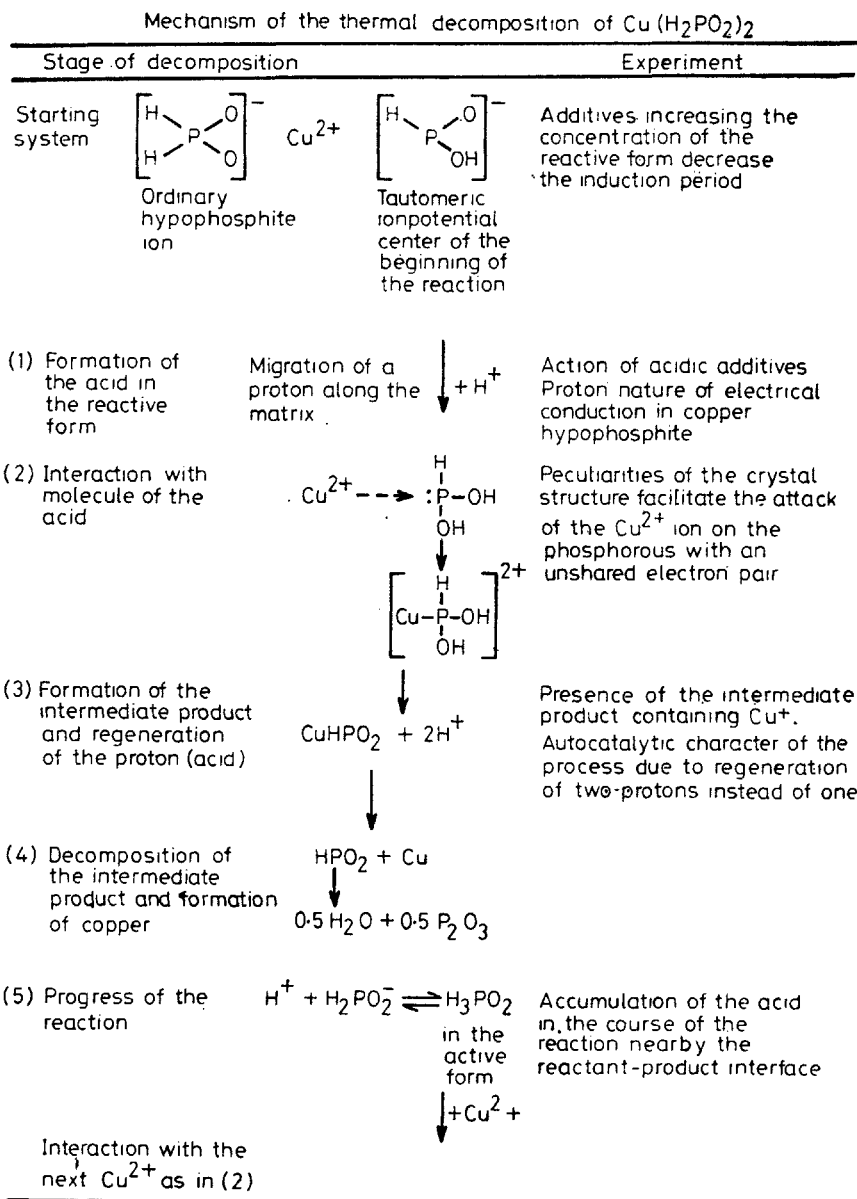


FIG 2 Mechanism of the thermal decomposition of copper hypophosphite.

amounts of defects and samples in which the amount of protons or anions in the active form is increased or reduced. The amount of defects in copper hypophosphite can be altered by doping, introduction into crystallization solutions of additives which raise or decrease the concentration of anions with three-coordinated phosphorus. Copper hypophosphite may be preliminary irradiated with ultra-violet light. Such a treatment leads to the formation of the acid.

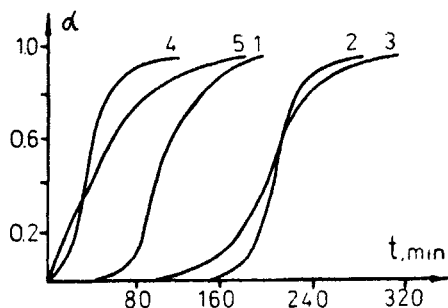


FIG 3 Kinetics of the thermal decomposition of copper hypophosphite grown from solutions with additives : 1—pure copper hypophosphite; 2—with an additive of alkali; 3—iron(II); 4—silver (I); 5—acidic sulphate-ion.

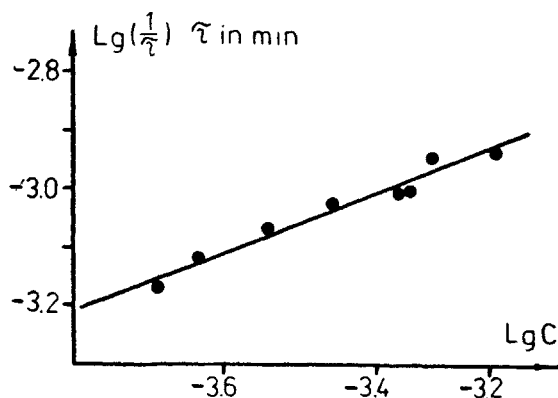


FIG 4 The concentration dependence of the nucleation rate  $1/\tau \text{ min}^{-1}$  ( $\tau$ — $t$  the time of induction period) on introduction of acid additives into a copper hypophosphite crystal (mole of the acid/mole of copper hypophosphite). The temperature of decomposition is  $50^\circ\text{C}$ .

Fig. 4 shows a dependence of the nuclei formation rate on the concentration of an acid additive introduced into the crystal.

The available different methods of the control enable the development of technologies on the basis of the studied reaction and provide the control of practically important properties of the starting substance. The stability of copper hypophosphite may vary over a broad range. For example, the substance can be decomposed at  $50^\circ\text{C}$  without induction period or with an induction period of 3 hours. The times of the decomposition with an observable rate in both cases amount to half an hour.

As regards the rate of nuclei growth or the rate of advance of the reactant-product interface of a topochemical reaction, this problem has been studied to a significantly lesser degree.

The proposal exists that the reactivity of a solid nearby the interface is elevated. The causes of this may be different, one being of a chemical nature. The resulting mobile products of the chemical reaction permeate into the unreacted regions and promote the decomposition.<sup>1</sup>

Looking at Fig. 2, i.e., mechanism of the thermal decomposition of copper hypophosphite, it is found that the interaction of a molecule of phosphorus acid and a copper ion gives the products: metallic copper, phosphorus trioxide, water and two new protons or two new molecules of the acid. It can be suggested that the forming in growing number molecules of hypophosphorus acid would reduce the next copper ions. The reaction proceeds by a chain mechanism.

The distribution of the acid concentration nearby the interface has been investigated using special microphotometric and electrophysical techniques. The main results are such.

The distribution of the acid nearby the interface in the direction normal to the interface is shown in Fig. 5 for the case of the decomposition of a crystal. It is seen that the concentration is maximal at the interface, the concentration is increased at a distance of  $100\mu\text{m}$  from the interface. The width of the distribution increases with increasing temperature. Great quantities of the acid permeate into the crystal. The interface advance rate increases.

Fig. 6 shows a schematic diagram of the decomposition of copper hypophosphite on a support. The acid from the reacted region of the layer diffuse into the unreacted region and promotes the decomposition. In order to control the reactivity of the substance nearby the interface, one should regulate the permeation of

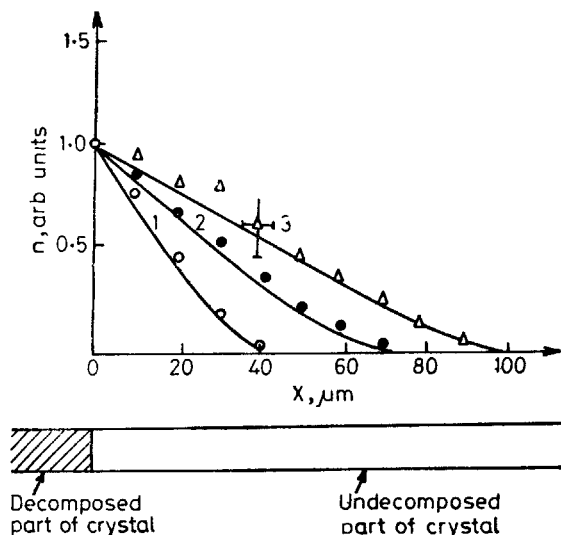


FIG 5 Distribution of the acid nearby the interface in the case of thermal decomposition of copper hypophosphite single crystals: 1—at a decomposition temperature of 296 K, 2—300 K, 3—308 K.

the acid into the unreacted region. If the support is not neutral and reacts with the acid, the acid diffusion in the layer can decrease. The reactivity can also decrease.

The width of the acid distribution depends on the preliminary saturation of the support with an acid. Then at the same temperatures the distribution width is larger, as seen in Fig. 7. In the case of supports with a high acidity great quantities of the acid diffuse into the unreacted regions of the layer. The rate of advance of the interface increases with increasing acidity.

Fig. 8 shows the dependence of the interface advance rate on the acidity of a support. The rate of advance may change 100 times.

Thus, the finding of factors that determine the reactivity of solids in topochemical reactions and the control of these factors is an effective way of controlling the second topochemical parameter—the interface advance rate.

What are the applications of the obtained results in technology? As an example, consider the technology of metallization of dielectrics. The topochemical decomposition of layers of copper hypophosphite is used in new technologies to copper dielectric surfaces with copper.

Fig. 9 gives schematic representations of the traditional palladium method of metallization and of a new technology. To carry out the palladium method of metallization of a dielectric it is necessary to treat its surface with a number of solutions. Originally, one should adsorb a tin salt on the dielectric surface, hydrolyze it. The hydrolysis product reduces palladium from the solution, particles of metallic palladium are formed. These particles are catalysts for the precipitation of copper from the solution.

The new technology, instead of successive treatments in solutions, uses the decomposition of a layer of copper hypophosphite on the dielectric surface.<sup>2</sup> The decomposition products show electrical conduction.

The use of a topochemical solid state decomposition in this technology gave rise to the process equipment of a new type—conveyor. A supporter to be metallized is placed on a conveyor, covered with a layer of copper hypophosphite and moves through the zone of thermal treatment. The decomposition starts on one

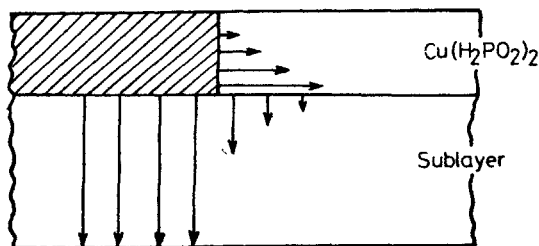


FIG 6 Schematic diagram of diffusion of the acid from the decomposed part of the layer on a support.

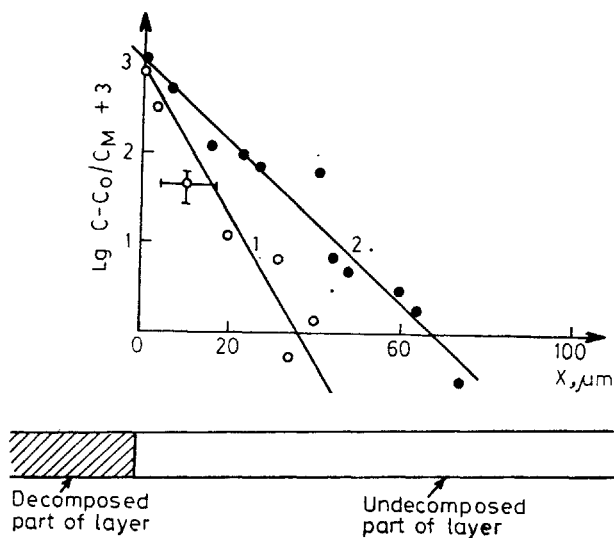


FIG 7 Distribution of the acid nearby the interface in the case of decomposition of a copper hypophosphite layer at 363 K on supports: 1—starting support, 2—treated with 50% phosphoric acid. Electrophysical data.

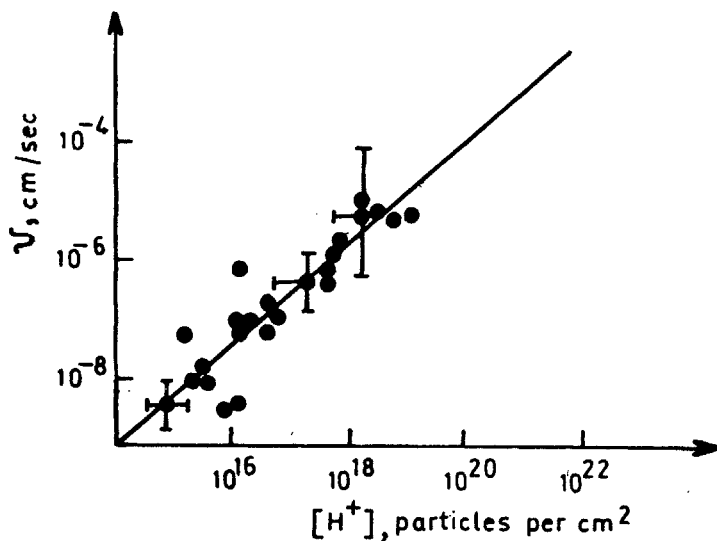


FIG 8 The rate of advance of the interface in the decomposition of copper hypophosphite layers vs. the concentration of an acid ( $H^+$ ) per  $cm^2$  of a support. The temperature is 363 K.

side of the plate, the interface decomposed—undecomposed part of the layer moves to the other side of the plate. The interface advance rate, at first sight, is of abstract character. In the given case, it is identical to the main technological

## Flow diagrams of metallization processes of dielectrics

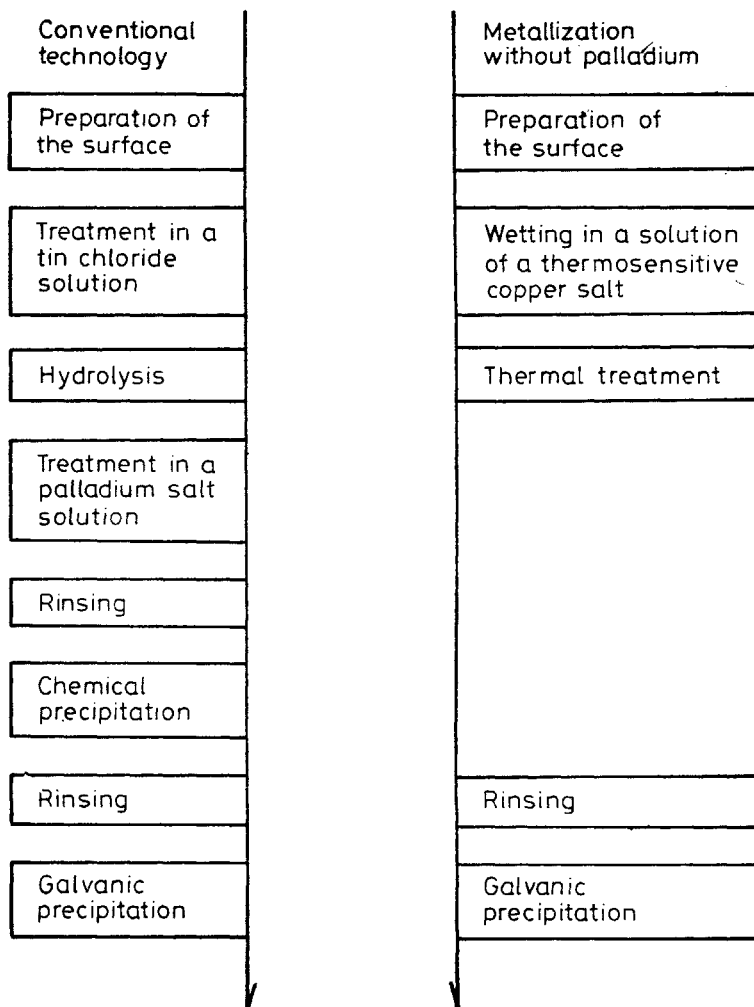


FIG 9 Flow diagram of metallization process of dielectrics.

parameter—the rate of motion of the conveyor. The productivity of the assembly line can be increased in the same way as the kinetic parameter in question—the rate of advance of the interface.

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