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ELECTROCHEMISTRY AND OTHER PROCESSES OF CHEMICAL TECHNOLOGY

Fabrication of Coatings Based on Epoxy Resins for Environmental Protection of Microelectronics

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Abstract—Modified coating for protection of microelectronics from external effects, including radiation, was created on the basis of epoxy resins. The coating was produced with a modifier, thioalkaphene B, containing polysulfide derivatives of ortho-tert-butyl phenol. The mechanism of its action was explained. The technology for coating deposition was tested on an industrial automated line; the thus protected semiconductor devices successfully passed tests in extreme working conditions.

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The quality and properties of modern microelectronics are determined by the forward and reverse voltages and forward and reverse currents. The irradiation and external factors are the main reason for the increase in the reverse current of a *p–n* junction, which reduces the intensity of electromagnetic signals passing through a device. To diminish the extent of these and other negative external factors, semiconductor devices are protected by coatings.

Coatings based on an epoxy resin, distinguished by mechanical strength and simplicity of deposition, have found mass practical application [1]. In addition to providing necessary mechanical properties of a coating, it is necessary to guarantee that requirements to devices working under extreme conditions should be satisfied: a device must be stable against moisture and temperature drops, be chemically inert, and leave unchanged parameters of electromagnetic signals passing through the device under increased radiation conditions.

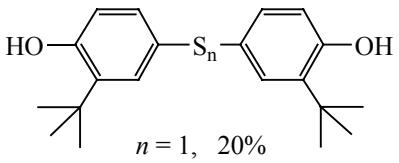
The problem of the radiation protection of microelectronics was solved in one of patents by using epoxy resins containing a large number of aromatic rings [2]. In this case, a wall of interacting electrons, ordered by aromatic rings, appears on the way of radiation. The wall creates conditions for an ordered redistribution of the energy flux and reduces its energy via acceleration of electron motion in the rings of aromatic compounds [3].

It was found that a part of shortcomings inherent in coatings based on epoxy resins can be eliminated by raising the adhesion of epoxy compounds to metals from which current leads and places at which thee are soldered to devices: tin, copper, silver, aluminum, and alloys of these. A good adhesion to these metals is provided by introduction of compounds containing a chain of six and more sulfur atoms into the epoxy resin formulation, followed by heating of the composite [4]. The good moisture resistance of the coatings formed on semiconductor devices provides stability of electromagnetic signals passing through the devices and makes longer their stable operation.

A set of additives is suggested, which enables a reliable protection of modern semiconductor devices from external effects when used to fabricate a protective coating [5]. For example, three additives are introduced into the epoxy resin prepared on the basis of dihydroxybiphenyl: (i) HMP8 phenolic antioxidant (methyl phenol sulfides), (ii) radiation protection additive,

and (iii) morpholine disulfide (Actor R) capable of providing, under certain formulation heating conditions, adhesion of a protective coating to the conductor metal. A thermal polymerization of a formulation of this kind yields a compound that is suitable for protection of the semiconductor and solder and is distinguished by high moisture resistance, good adhesion to metals, and stability against heating.

A domestic product was used to reliably protect semiconductors in stead of three imported compounds. It simultaneously contained aromatic rings, and a polysulfide chain, and a fragment of a phenolic antioxidant capable of interaction with epoxy resins. All these three requirements are satisfied for he thioalkaphene B stabilizer (TAB, the abbreviation suggested by Khimpolymer Research Institute for polymer stabilizers). The stabilizer is obtained by interaction of 2-*tert*-butylphenol with sulfur monochloride in the presence of dimethylformamide. The composition of the resulting products has been thoroughly studied [6]. Its main component (70%) was a mixture of di-and polysulfides:



$n = 1$, 20%
$n = 2$, 50%
$n = 3$, 10%
$n = 4$, 10% (1)

In addition to the polysulfides of specified structure, two groups of compounds (10% each) containing one or two polysulfide chains were found in TAB.

It has been found previously in a study of the thermal-kinetic properties of the components of TAB that the monosulfide it contains [compound (1), n = 1, 20% in the mixture] is an ordinary antioxidant additive. The rest of the components [di- and polysulfides, compounds (1) with n = 2, 3, 4] belong to a newly discovered group of phenolic polymer modifiers [7]. Compounds of this kind behave at room temperature as ordinary antioxidants, but heating results in reaching the temperature of their decomposition into radical species acting as oxidizing agents. The thermal decomposition point of the disulfide [compound (1) with n = 2, the main component of TAB] is 160–180°C [8]. A noticeable decomposition of tri- and polysulfides [compound (1) with n = 3, 4] is observed in the same temperature range.

For example, thermolysis in the course of coating fabrication leads to an oxidative burst of the TAB components, as shown in Scheme 1. This process is also typical of other phenolic modifiers and ultimately converts these into antioxidants. If a polymer is in the environment of the radical species formed in this process, the species react with the polymer and chemically modify its properties. This gives a new polymer having improved physical-mechanical properties and containing a fragment of a phenolic antioxidant [9].

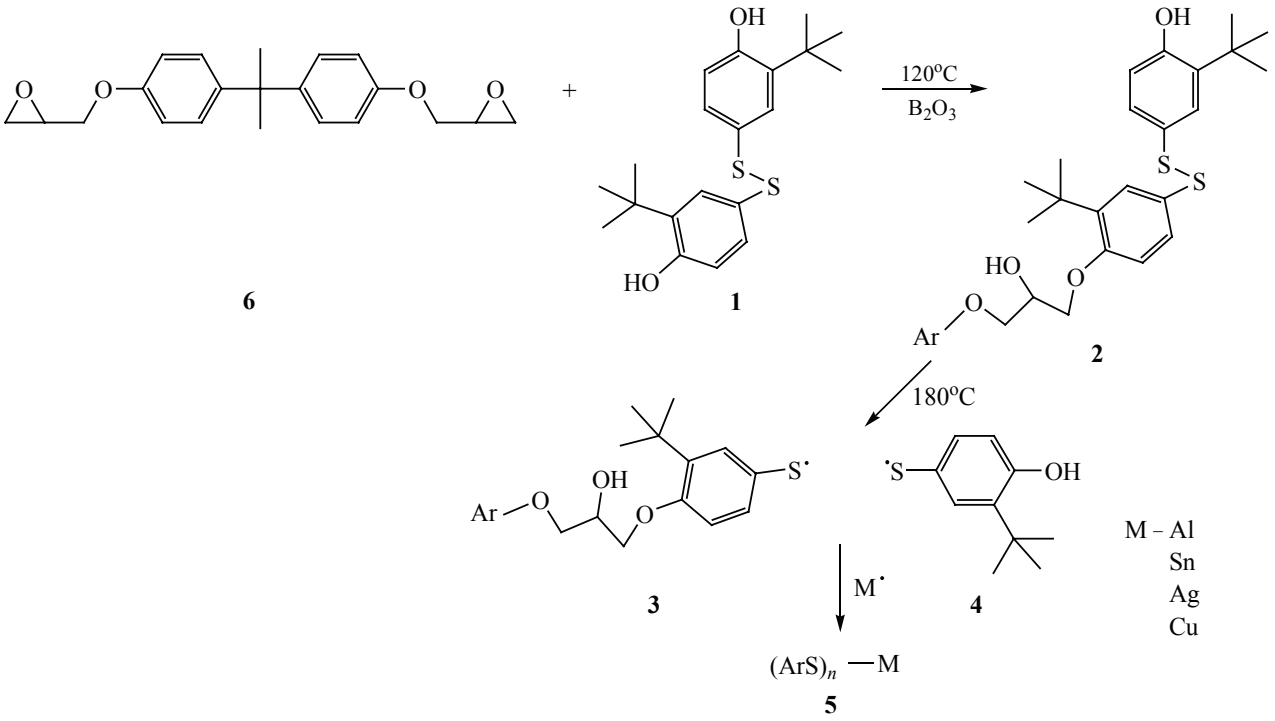
However, there is another, also highly important case, when a metal consists the environment of the "exploded" modifier. Its fragment can be "linked" to the metal, with an adherence layer thereby formed [4].

The TAB stabilizer **1** interacts with ED-20 epoxy resin **6** or ED-24 (the resins are interchangeable) by various schemes, depending on the nature of a catalyst and on the extent to which the formulation is heated. In the first stage, in the presence of the catalyst (boron oxide), the reaction of esterification of the phenolic group having only a single tert-butyl group in its environment readily occurs at a temperature of 120°C to give ether **2**.

Further cleavage of the disulfide bridge in compound **2** is observed in the range 160–18°C to give radical-containing compounds **3** and **4**, which presumably interact with the conductor metals and form a solid layer adhering to the metal and solder to the device, to give product **5** with a probable structure $(ArS)_n$–M, where M is the metal that closes the gap between the protection polymer and the conductor and thereby precludes penetration of moisture into the gap during operation of the device.

These reactions occur in a thin layer on the surface of chip, with area not exceeding 2–4 mm^2. In the first stage, at a temperature of 120°C, a solid oligomeric compound **2** is formed. It is easily detachable from the substrate to form a free space between the protective layer and the device, because no firm adherence layer is formed under these conditions. No adhesion could be observed at this temperature even upon a very prolonged keeping. The reason is that the process in which radicals necessary for obtaining an adherence layer is slow. The radicals are fully "caught" by the TAB stabilizer components. Therefore, it is necessary to take the stabilizer in an amount of 2.4%, which substantially exceeds that recommended (0.05–0.5%) for polymers in industrial practice, and perform the protection fabrication process itself at a considerably higher temperature (180°C).

Scheme.



6 **1** **2** **3** **4** **5**

The formation of an adhesion layer solves one of the most important problems of microelectronics, its moisture protection. The above transformations have no effect on the initial electrical characteristics of a semiconductor device, with its negative characteristic, reverse current, reduced by a factor of 1.7.

EXPERIMENTAL

A batch of high-voltage rectifier piles of KTs113A-1 diodes (1700 pieces) was divided into two parts before being protected. The firs part was protected and then encapsulated with EKLB epoxy compound containing ED-20 epoxy resin and a polymerization catalyst, boron oxide). To these was added (in a 100 : 2.4 mass ratio) TAB modifier. The second part was protected and encapsulated with EKLB epoxy compound without modifier. The protected articles were simultaneous subjected to hot-curing polymerization in a drying oven in the following mode: 1st stage, temperature 120°C, keeping for 6 h;

Properties of the protection of a *p–n* junction of control and test groups of semiconductors in their manufacture on an automated production line

Content of TAB in ED-20 epoxy resin, %	Median leakage current J_{rev}, 10^{-9} A		Median enlargement ratio	Percentage of rejects upon irradiation, %	After storage for nine months	
	before irradiation	after irradiation			Median leakage current J_{rev}, 10^{-9} Å	Percentage of rejects, %
0	4.45 min: 2.7 max: 19.7	7.5 min: 3.0 max: 16.0	1.68	0	6.4 min: 3.2 max: 74	14
2.4	5.7	8.5	1.49	0	5.45	0.5

2nd stage, temperature 180°C and keeping for 14 h. After being protected the articles were potted with the same compound and subjected to polymerization in a drying oven in the mode: 1st stage, temperature 85°C and time 4 h; 2nd stage, 120°C and 7 h; and 3rd stage, 180°C and 15 h. Formation of the protective layer formed in this way provides a high reliability of microelectronic devices in extreme working conditions. The finished articles were irradiated with 2.4 MeV electrons (electron beam current 0.3 A) for 3 h 30 min.

After a control measurement of their electrical parameters, the articles were stored at room temperature for nine months, after which the parameters were again measured. The measurement results are listed in the table. The reverse currents in these devices are noticeably lower than those in the control group. In the articles produced with TAB modifier, the reject percentage decreased from 14 to 0.5%. The reverse current Jrev in the modified samples decreased, compared with the control group of devices, by approximately a factor of 1.7 on average (from 0.012 to 0.007 μA).

No rejects were found in devices with a modified coating after their storage for 12 months. The above transformations were simulated in parallel in cuvettes made of various metals. No adhesion transformations were observed at 120°C: the polymeric compound (2) being formed was easily detached from the mold. In the subsequent stage performed at 180°C with TAB-containing compounds, the adhesion of the new polymer (5) being formed to the cuvette material was so high that the cuvettes had to be eliminated by abrasion to extract their contents.

Thus, a number of problems could be solved: (i) the reverse current in the semiconductor could be reduced, which improves its quality, and the effect of irradiation could be substantially diminished; (ii) the solid adhesion layer on the semiconductor surface precludes penetration of moisture into microcracks of the protective coating, which leads to a stable and prolonged operation of the device; and (iii) the initial properties of semiconductor devices are stabilized in their storage and operation and the commonly used moisture protection of devices becomes unnecessary.

Industrial tests of the new method for protection of microelectronic devices have been successfully performed at Novosibirsk plant of semiconductor devices on an automated production line [10]. The working capacity of these devices was tested under prolonged-storage conditions with the ordinary package containing a moisture absorber and in extreme working conditions.

It should be noted that the chemical modification considered here is promising not only for microelectronics, but also for production of TAB-modified polymers for articles insensitive to solvents and water. These polymers also better withstand mechanical treatments [11].

CONCLUSIONS

(1) A thermoreactive-resin formulation containing an epoxy resin, polymerization catalyst, and modifier (thioalkaphene B) was suggested for producing a coating for protection of microelectronic devices from the environmental exposure.

(2) Technological conditions were found for thermal polymerization of the formulation for producing a protective coating for semiconductor devices, with the subsequent formation of an adhesion layer.

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