

Investigation of the adhesive properties of composites based on polyimide varnish and copper oxide, boron nitride and technical diamond powders

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Abstract

The article describes the preparing process for composites with a polyimide varnish PILK-2B matrix, which filled with particles of technical diamond, copper oxide, cubic boron nitride and hexagonal boron nitride for use in redistribution layers during chip packaging. Article show the results of the adhesive properties study for these composites with various fillers in relation to alkali glass and ST50 sitall substrates using the pull-off method. The measurement showed that the maximum adhesion to sitall and glass substrates is characteristic of the composite based on cubic boron nitride. It is 20.97 MPa and 20.11 MPa, respectively. Composites based on technical diamond and hexagonal boron nitride show lower adhesion – 17.48 and 18.03 MPa for sitall, 17.27 and 16.84 for glass. The material based on copper oxide show a significant difference in adhesion for sitall and glass – 14.78 MPa and 19.65 MPa, respectively. In addition, the article presents the results of composite processing using infrared nanosecond laser ablation to obtain structures in the form of traces and cylinders (contact pads) of various sizes. Cubic boron nitride based composites show clearest pattern with minimum line/space parameter of 25 µm and minimum delamination. Composite based on hexagonal boron nitride show the worst result with the maximum number of damages and flakes during laser treatment.

Keywords

3D integration, packaging, polyimide, redistribution layer

1. Introduction

Despite the wire bonding technologies continue to occupy a dominant position in the semiconductor packaging market [1], their share is decreasing every year. The first

reason for this is the reduction in pitch and pad size of modern integrated circuits. This requires the use of wire with a small diameter of 12–18 µm [2–5]. Also, in modern integrated circuits the contacts are increasingly arranged over the chip area in the form of a matrix, which complicates chip mounting using wire bonding.

As result wire bonding is being replaced in a number of applications by advanced packaging technologies. One of them is the rapidly developing wafer-level packaging (WLP).

Compared to wire bonding, WLP is a group technology [6–8]. Connection of the die pads with the package pad for WLP technologies are carried out by means of a redistribution layers that formed over the entire surface of workpiece. Some types of WLP technologies make without soldering and welding processes [9]. It achieves a number of positive effects, such as reducing contact resistance and eliminating the formation of intermetallic compounds [10].

Redistributive layers (RDL) are the main element of any packaging technology at the wafer or panel level. These layers include metal (usually copper) conductors and a thin dielectric formed by additive methods with microvias between the conductive layers. Polymer materials, which are characterized as photosensitive [11–13] or easily removed by laser or plasma etching [14], act as the RDL dielectric. These are polyimide, polybenzoxazole, benzocyclobutene, and epoxy heat-resistant photosensitive resins such as SU-8 [15].

Wafer level packaging technology allows using of any die size [16, 17] with pads made of any material [18]. However, the most significant property of WLP over traditional wire bonding is a reduction in package dimensions [19–21].

In addition to WLP technology, redistribution layers can be applied in several other types of advanced packaging technologies, for example in embedded die packaging [16, 22], in Fan-In chip scale packaging [23] and in many interposer technologies.

Redistributive layers line/space dimensions in WLP technologies can reach 5–10 μm for semiadditive technology (SAP), and from 2–5 μm for dual damascene technology [24, 25]. At the same time, line/space equal to 2 μm can be achieved both on traditional polymer RDL and using hybrid WLP technology, which assumes the presence of back-end-of-line (BEOL) commutation layers with silica or silicon nitride as a redistribution layer dielectric [26, 27].

Thanks to specialized epoxy molding compounds (EMC) and modern semiconductor molding equipment, the thickness of the final WLP package can also be only a few tens of microns larger than the thickness of the die [28]. Also FOWLP use to manufacturing of two-dimensional and three-dimensional systems in package [9, 25].

However, FOWLP technologies also have challenges. Two of them stand out the most. The first is small heat dissipation due to the relatively low thermal conductivity for the compound and for the dielectric of redistribution layers [25]. Second problem is a high risk of polyimide delamination off the substrate due to thermomechanical stresses. Delamination is most relevant for processes using electroless surface treatment, when the material is simultaneously exposed to aggressive reagents and elevated temperatures.

An interesting solution to these problems it is the use of composite dielectric for redistribution layers. These composites consist of a heat-resistant polymer, such as polyimide, and micro or nanoparticles of inorganic filler [29, 30]. Such RDL could combine the advantages of plastic organic dielectrics [31] with some advantages of inorganic BEOL layers, such as chemical resistance, high thermal conductivity, and low thermal expansion [28, 32].

Epoxy-molding compounds (EMC's) are composite examples where the introduction of non-organic material filler with low coefficient of thermal expansion (CTE) and high thermal conductivity into organic dielectric caused a significant decrease in thermomechanical strain. EMC is composite materials with 80–90 % of filling, where filling significantly reduce the CTE of the material from $(30\text{--}50) \cdot 10^{-6}/^{\circ}\text{C}$ to the order of $8 \cdot 10^{-6}/^{\circ}\text{C}$ [33, 34]. But despite the existence of interposers make from EMC, this material class not use for RDL due to the presence of large filler particles (tens μm), low temperature resistance and problems with the formation of a pattern in the material.

The underfill materials use composites with a smaller filler particle size than for EMC. The particle size for these materials reaches hundreds of nanometers [35–38]. But low glass temperature resin and the low percentage of filling can be an obstacle to using these materials as RDL dielectric.

The above examples show that the introduction of filler into the polymer actually leads to a decrease in thermomechanical stresses and increase the thermal conductivity of the material. However, the existing variants of filled composites are not suitable for use as an RDL dielectric. The solution for this problem is to create composites based on traditional RDL materials (for example, polyimide) using sufficiently fine fillers. There are some examples of studies in area of composites based on traditional RDL dielectrics [29, 30, 39–42]. The purpose of these studies is to produce homogeneous composites for RDL and measure their parameters without reference to specific technological processes of pattern formation. However, during the formation of a microvias and cavity's pattern in the RDL layer, the effect on the material may be more aggressive than during further operation of the device.

This study considered the process of obtaining a dielectric composite for RDL and the subsequent process of forming a pattern in this composite by infrared (IR) laser ablation in conjunction. The study made it possible to establish the influence of the filler parameters in the composite (filler material, shape and particle size) on the subsequent laser ablation process. Also this research allows comparing the adhesion for composites before laser ablation and behavior of materials (delamination, carbonization) during the ablation process. The study also establishes the optimal composition of the RDL dielectric in terms of ensuring maximum adhesion of the dielectric material to the substrate after the pattern formation.

2. Description of materials used

For WLP technologies, polyimide is the most common RDL dielectric due to its high chemical resistance, heat resistance, plasticity, accessibility, and relative ease of processing. Therefore, polyimide was chosen as the basis for the preparation of composites in this work.

For the preparation of the composite material we used polyimide varnish PILK2V [43]. PILK2V is a solution of polyamide acids based on aromatic diamine and aromatic tetracarboxylic acid dianhydride in N,N-dimethylformamide or N,N-dimethylacetamide. The specified varnish after curing is characterized by a high specific volume resistance of the order of 10^{16} – 10^{17} Ohm·cm, which contributes to its wide application in the electronic industry for the creation of integrated circuits and semiconductor devices.

When determining the list of inorganic fillers used in the study, the main parameters was CTE and thermal conductivity. Attention was also paid to the chemical resistance and parameters of the interaction of the material with infrared laser radiation (since laser ablation is the easiest way to obtain a precision pattern in composite materials with inorganic fillers). It also based on works where similar compounds were studied [29, 30, 38–44]. As a result, fillers based on cubic and hexagonal boron nitride (materials actively studied as EMC fillers), as well as technical diamond (due to the stability of properties, high thermal conductivity and numerous studies of diamond composites for various purposes [45]) were selected for the study.

Redistribution layers often become the basis for the formation of various passive elements for a packaged chip. These are usually antennas or other microwave elements, but there may also be elements of functional electronics. For this reason, the authors of this paper decided to investigate not only dielectrics as fillers, but also materials that can become the basis for planar functional elements. The work used the most accessible of such materials, for which the nature of interaction with IR laser radiation is also known – copper (II) oxide. Table 1 shows the parameters of the using fillers.

In addition to the possibilities of laser micro-processing to form a pattern in composites, the adhesion of the

obtained composite materials to separation was also investigated. The study was carried out on two types of substrates: sitall (the composite was applied to the polished side) and alkaline glass.

Glass was chosen because of the active spread of the idea of glass substrates in the field of packaging, because of the use of glass as a temporary carrier in WLP technologies, as well as because of the transparency of glass for laser radiation. The latter made it possible to minimize damage to the substrate at the material removal sites and, thus, increase the accuracy of measuring the profile of the resulting structures.

Sitall used as the opposite to glass in order to determine how precisely, without affecting the substrate, it is possible to remove the composite. In addition, the reason for choosing sitall was accessibility, minimal CTE and low roughness on the polished surface.

Boron nitride (BN) powders with hexagonal (graphite type) and cubic (sphalerite type) crystal structures, technical diamond powder and CuO powder were used as varnish fillers.

When preparing the samples, the task was to produce a composite material with the maximum possible filler content so that the resulting composite had as low CTE as possible and as much thermal conductivity as possible.

To describe the filler content in polymer matrix-based composites for electronic applications, the percentage by weight (wt.%) is most often used as an indicator of the inorganic particle content. However, percentage by volume is a more objective indicator for describing the filler content in composites, since it does not depend on the density of the filler material. Widespread of weight percentage property is the result of the one type of filler domination in electronic applications composites. It is the spherical silica, for example using in epoxy molding compound and epoxy based underfill materials.

Nevertheless, spherical silicon dioxide is not always the optimal type of filler for an electronic compound due to its relatively low thermal conductivity and laborious spheroidization process. In addition, polyimide varnish has a viscosity and chemical structure different from epoxy. Therefore, the nature of its interaction with the filler differs from epoxides. For example, functional group in epoxides it is active oxirane group. However, in polyimide functional group is stable imide cycle group.

Table 1. Parameters of the using fillers

Material	Declared particle size (μm)	Thermal conductivity ($\text{W}/(\text{m}\cdot^\circ\text{C})$)	CTE ($\text{ppm}/^\circ\text{C}$)	Density (g/cm^3)
Polycrystalline technical diamond	1–3	~60 [46]	~3.2 [47]	3.53
Polycrystalline cubic BN [48]	1–3	56	4–6	3.49
Hexagonal BN	<50	220 parallel to the c axis and <5 perpendicular ; for composites depend on particle orientation – from 0.42 to 120 [49]	–2.7 parallel to the c axis, 38 perpendicular [50]	2.10
CuO	<50	69–76 [51]; 33[52]	5.1–7.7 [53]	6.315

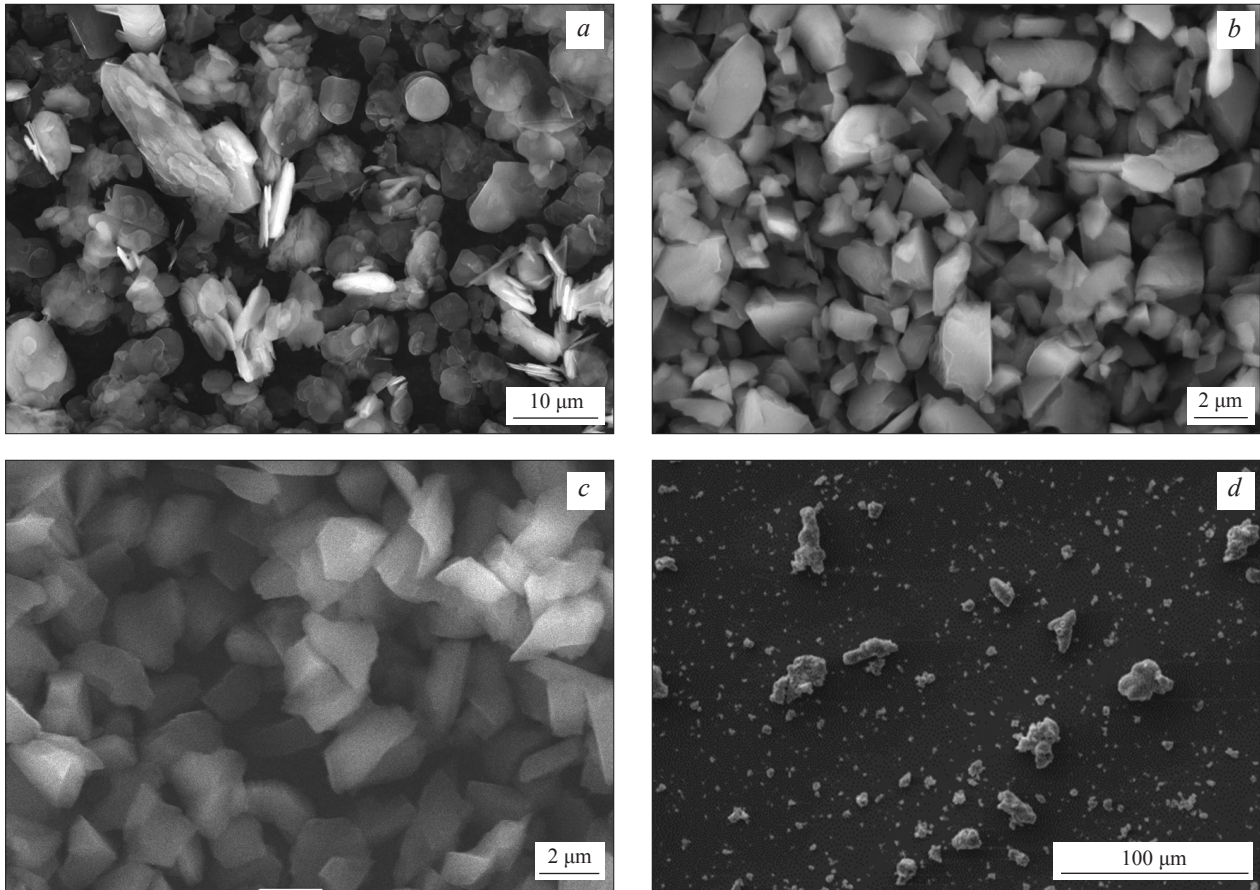


Figure 1. SEM images of boron hexagonal nitride powder (a), cubic boron nitride (b), technical diamond (c) and copper oxide (d)

High thermal conductivity of the filler is a very important property, since the simplest method of making a pattern in a polyimide-based composite is laser treatment. Rapid heat removal from the treatment area is essential for the laser ablation process. For example, laser ablation of copper from the surface of polyimide is very difficult process. Polyamide heats up quickly under the treated surface due to its low thermal conductivity. At the same time, on the surface of foil-clad polyimide, rapid heat dissipation along the heat-conducting copper foil leads to the need for lengthy processing. As a result, deformation of the polyimide occurs in the processing zones.

For the reasons stated above, in this study, we use for filler different materials with high thermal conductivity. Therefore, we use both parameters to characterize the filler content in the manufactured compounds. It is percentage by weight (wt.%) and percentage by volume (vol.%).

In experiments, we added filler to the polyimide stepwise, with a gradual increase in its mass content in the composite. Experiments showed that the maximum concentration for cubic boron nitride filler is ~60 wt.% (30 vol.%), for hexagonal boron nitride powder ~41 wt.% (24.86 vol.%), for technical diamond ~62 wt.% (31.61 vol.%), and for copper oxide powder ~64 wt.% (21.96 vol.%). When the specified percentage of fillers was exceeded by weight, the studied composite materials rapidly increased their viscosity, and agglomerates

of polymer-free particles began to form in them, which prevented the introduction of large proportions of fillers. Another problem was that it became extremely difficult to apply too viscous materials to the surface in the form of a thin layer, which requires the technology of manufacturing redistribution layers.

The difference in the maximum mass fraction in the composite for various fillers may be due to the shape and particle size of these materials. Figure 1 shows SEM images of particles of each of the fillers used.

Figure 1a shows that the hexagonal boron nitride (HBN) is characterized by a large variation in particle shape and size. Particles have a lamellar (scaly shape) and are randomly oriented in the composite, which provides them with a less dense package than in the cases of other powders.

Granulometric analysis showed that HBN particle size range was from 0.1 µm to 100 µm. All granulometric analysis results for material are consistent with each other. The graph of the particle size for HBN is sloping. Particle size characterized of distribution maximum in 9.0–9.5 µm. In addition, the proportion of particles with sizes of 1.6–3.7 µm and 21.5–34.9 µm is large. Figure 2 show granulometric filler particles distribution for hexagonal boron nitride.

Cubic boron nitride (CBN) and technical diamonds have a smaller variety of shapes and particle sizes than

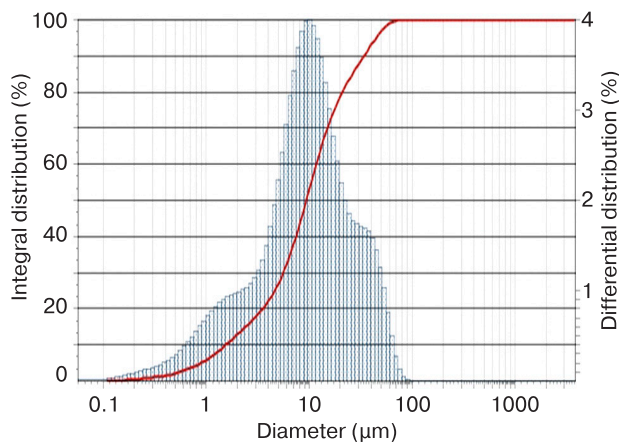


Figure 2. Particle size distribution of filler for hexagonal boron nitride

hexagonal boron nitride. Their particles have the shape of slightly elongated fragments (microcrystals) — Figs 1b and 1c.

Granulometric analysis showed that the particle size of CBN and diamonds is similar, as is their shape. Particle range for both materials is from 0.1 μm to 8 μm . All granulometric analysis results for CBN and diamond are consistent with each other. The distribution has two peaks for both SBN and diamond. The first small peak is at particle size of 0.2–0.3 μm . The second large peak is at particle size of 2.0–2.5 μm . Figures 3 and 4 shows the granulometric distribution of filler particles for cubic boron nitride and diamond, respectively.

Copper oxide particles are less uniform in terms of shape and size compared to boron nitride and diamond, but they have a complex shape with smoothed edges, close to ellipsoidal or spherical – Fig. 1d. Due to the absence of sharp edges, the gaps between large particles are more easily filled with smaller fragments of material when mixing the composite, which in theory increases the packing density. At the same time, the developed surface of the filler can interfere with the distribution of the filler in the compound and reduce the percentage of filling.

Figure 5 show granulometric analysis of copper oxide. Analysis shows the presence of two peaks of almost the same height. This indicates the presence of two equal fractions. The first fraction has a size of about 0.7 μm . The second fraction has a particle size of about 25 μm . The maximum particle size for copper oxide, according to the analysis results, is about 60–70 μm . There are nanometer particles with dimensions less than 0.1 μm .

The composite material with filler in liquid form covered the surface of two type substrates

The first type of substrate had dimensions of 48×60 mm. Material of this substrate is sitall, also named as citallic, glass ceramic, pyroceramic or ceramized glass. It is a fully or partially crystallized glass material with fine-grained and homogeneous crystalline structure based on Li_2O , Al_2O_3 , SiO_2 , MgO and other oxides. In this study, we used ST50-1-1-0,6 grade sitall substrates with one sided polishing.

The second type of used substrate had dimensions of 40×40 mm. Material of this substrate is alkali glass.

Before applying the composite coating, an optical profilometer examined the surface of both substrates. Figure 6 show the surface analysis result for glass and sitall respectively.

Roughness of glass and polishing surface of sitall is approximately the same. It is equal to 23–28 nm based on the results of several measurements of each type of substrate using an optical profilometer.

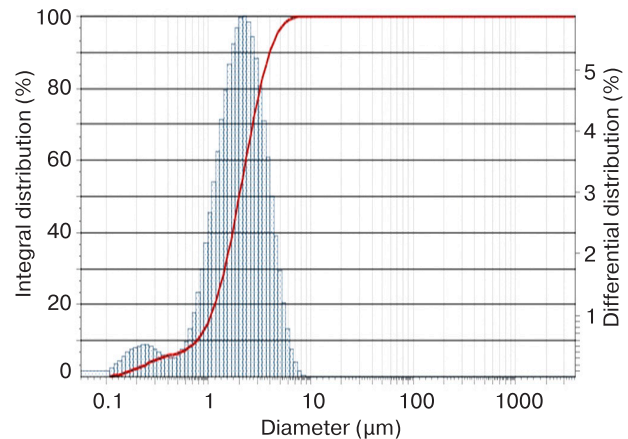


Figure 3. Particle size distribution of filler for cubic boron nitride

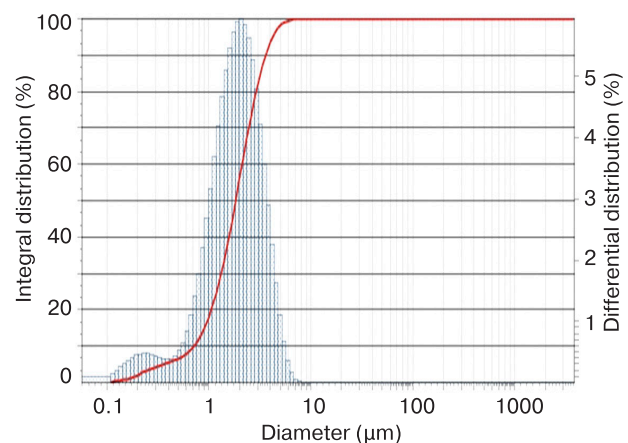


Figure 4. Particle size distribution of filler for diamond

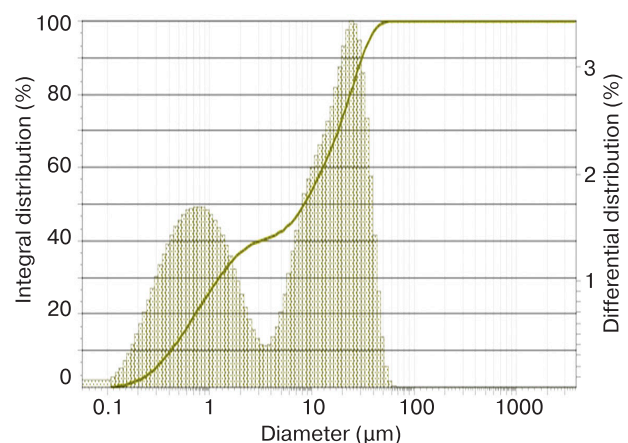


Figure 5. Particle size distribution of filler

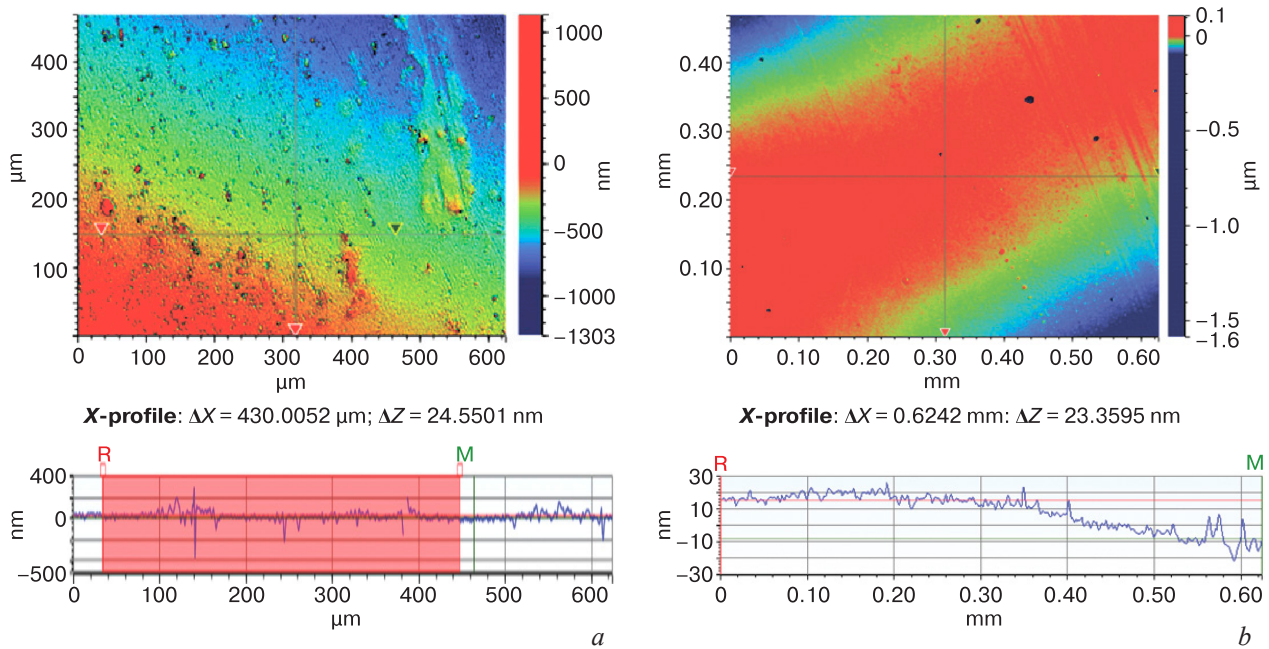


Figure 6. Images of the surface for the used substrates made of glass (a) and sital (b) from an optical profilometer

3. Formation of composite layer and adhesion measurement

In this study, only mechanical mixing of components was carried out to obtain composite materials. The powder was added to the polyimide varnish in several stages, after each stage, stirring took place in a planetary-type mixer SD-3088 with a rotation speed of the main axis of 1000 rpm and 380 rpm for additional ones.

Various methods have been tested for applying the composite to the surface of the plates: centrifugation, squeegee application, rolling with a polished glass rod. The best results according to the criterion of uniformity of coatings were shown by the methods of applying with a squeegee and rolling with a polished roller, since a significant problem when applying the composite by centrifugation was the agglomeration of the powder into large particles up to 400 μm in size (according to the results of optical analysis), as well as the uneven distribution

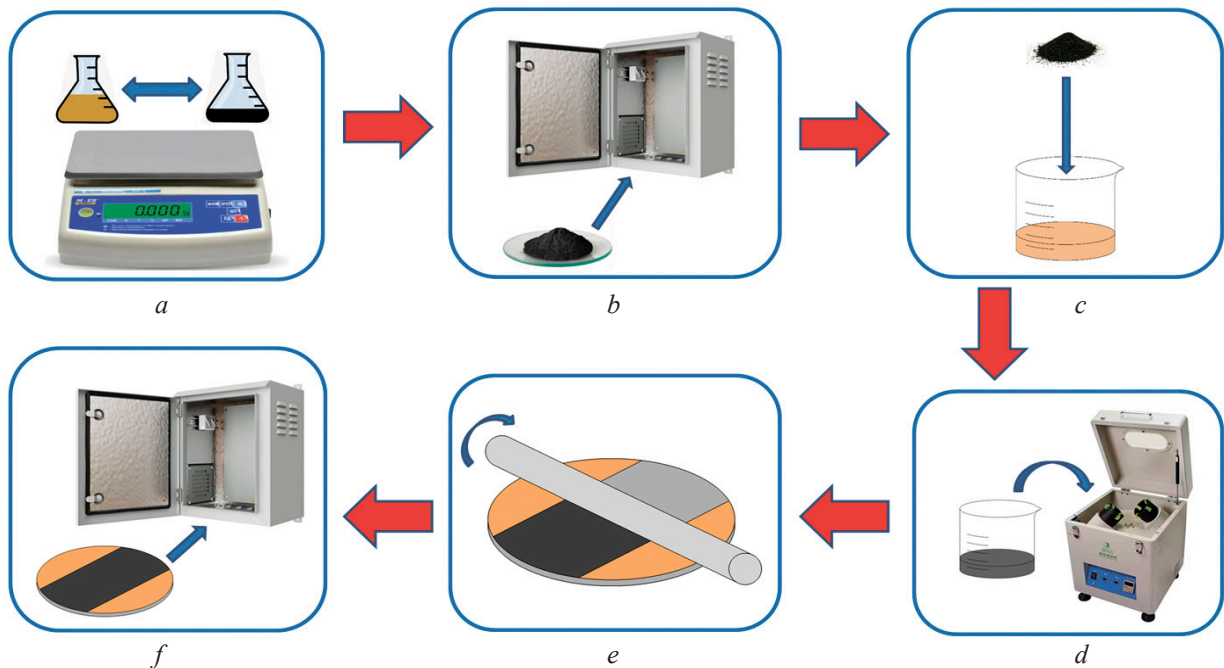


Figure 7. Algorithm of the technological process for the preparation of experimental composite samples: (a) weighing of components; (b) drying the powder in a thermoshaf; (c) adding the powder to a polyimide varnish; (d) stirring the composite in a mixer; (e) applying the composite to the plate by rolling a polished rod; (f) imidization of the applied composite in a thermal cabinet

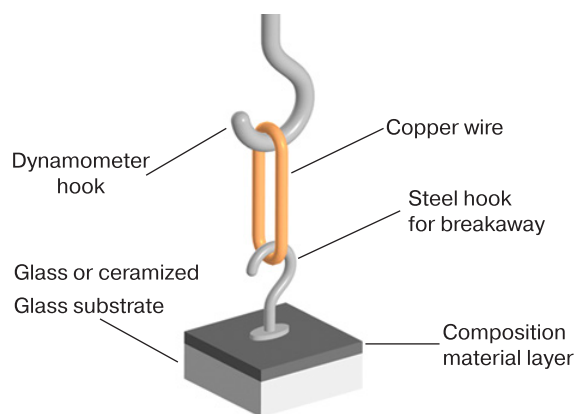


Figure 8. Structure of experimental samples prepared for adhesion tests

of particles over the surface of the plate. To reduce agglomeration, modification of the composite with a surfactant, namely decyl glucoside, was used. Ultrasonic treatment of the material before curing was also used to break down the agglomerates. Both approaches did not produce noticeable results.

After applying the polyimide varnish with the filler added to it, the imidization (curing) process was carried out in a thermal cabinet with stepwise heating to a curing temperature of 270 °C. The thickness of the composite material on all substrates ranged from 40 to 80 μm for a composite with hexagonal boron nitride and 50–60 μm for other types of composites. The height of the sides when applying the composite by rolling was 50 μm . The algorithm of the technological process of preparing composite samples using sieving powder through a sieve and rolling with a roller is shown in Fig. 7.

A special stand with a dynamometer measured the adhesion strength between composite and substrate. Objects for separation, which are steel hooks, were fixed on the material under study using VK-9 epoxy based glue. The area of contact of the composite material with the object for separation was 2.9 mm^2 . Figure 8 shows the structure of the experimental sample during the measurement of adhesive strength. There are ten measurements for each four composite types and for two substrates type. Total 80 measurements.

4. Results

Table 2 shows the numerical values of adhesion for all experiments and for each one of the four types of material on two types of substrate. In addition, table shows average adhesion values for all materials and substrate types.

The composite with cubic boron nitride showed the best results on both substrates: 20.11 MPa on a ST50 sitall substrate and 20.97 MPa on a glass substrate. The divergence between the adhesive strength values for two substrate materials is insignificant (4.1 %), which can be justified by an insufficient number of tests.

The composite with hexagonal boron nitride showed very similar adhesion results during separation for two substrates types of 17.48 MPa and 17.27 MPa. However, it is worth noting that in this case, almost all samples were destroyed in the body of the composite, and not at the boundary of the composite and the substrate. This suggests that the values obtained do not reflect the adhesive strength of the composite with the substrate, but the strength of the material itself. This explains why

Table 2. Results of measuring the adhesive strength of composite materials with ST50 sitall and glass substrates

Test No.	Separation force (MPa)							
	ST50-1-1-0,6 sitall substrate				Alkali glass substrate			
	Composite BN cubic	Composite BN hexagonal	Composite with technical diamond	Composite CuO	Composite BN cubic	Composite BN hexagonal	Composite with technical diamond	Composite CuO
1	18.76	16.03	19.90	18.84	21.45	26.71	14.57	36.35
2	19.54	16.59	14.66	27.43	26.93	18.47	29.68	23.88
3	20.37	18.48	23.47	12.73	17.56	14.84	22.53	19.10
4	18.66	16.71	26.68	9.74	26.32	17.89	20.31	26.32
5	18.85	18.22	10.66	15.99	23.44	15.01	19.53	30.04
6	23.76	23.90	17.37	14.12	17.81	14.97	14.12	7.97
7	20.19	17.19	9.52	14.74	22.13	16.32	8.66	12.53
8	19.82	18.26	21.71	12.10	20.42	16.50	15.12	12.50
9	21.27	12.82	23.08	9.22	22.52	16.45	7.30	16.41
10	19.87	16.66	13.25	12.93	21.17	15.49	16.60	11.37
Average value (MPa)	20.11	17.48	18.03	14.78	20.97	17.27	16.84	19.65

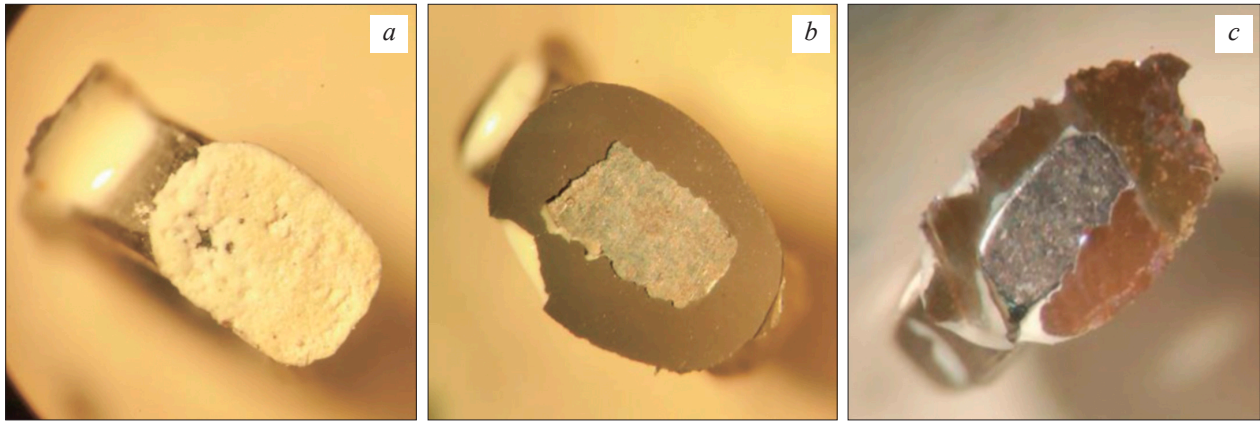


Figure 9. Traces of rupture of composite materials with a substrate: hexagonal boron nitride on glass (a); cubic boron nitride on glass (b); copper oxide on sitall substrate (c)

the values are so close to each other – the resulting divergence is 1.2 %. The actual adhesive strength between the substrates and this composite is higher than the values obtained. However, given that in the real structure of the redistribution layers, stress destruction occurs at the weakest point, which is not always the interface of materials, the values obtained will be fairly equated in importance to the rest, since they reflect the most vulnerable position in the studied structure from the point of view of strength. It is also worth noting that hexagonal boron nitride showed the worst parameters among all the composites considered in this study in terms of surface uniformity after application to substrates and curing.

The composite with technical diamond showed an adhesive strength of 18.03 MPa on a sitall substrate and 16.84 MPa on a glass substrate. The reason for the 6.6 % discrepancy may be an insufficient number of tests for greater convergence of results.

The composite with copper oxide demonstrated an adhesive strength of 14.78 MPa on a sitall substrate and 19.65 MPa on a glass substrate. The divergence is more than 24 %, which already indicates a significant difference in the data on the two types of substrates, even with a small number of tests. The reasons for this have not been discussed in detail in this paper. However, a possible reason for this effect may be the chemical interaction of copper oxide with OH groups on the surface of amorphous alkaline glass, which is more chemically active than the crystalline glass-ceramic sitall. Figure 9 shows photographs of traces of separation of some composite materials from the substrate.

4. Formation of microstructures on a composite material using an IR laser

For redistributive layers, adhesion of the dielectric to the substrate is not the only requirement. Another important parameter is the ability to form a pattern with small topological norms in dielectric.

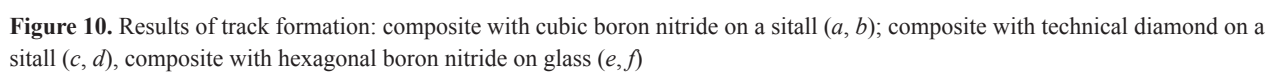
The traditional processes for making a pattern in an RDL dielectric are lithography for a photosensitive dielectric and etching for a non-photosensitive type of dielectric. However, due to the presence of a large amount of filler in composite RDL dielectrics, both of these processes are difficult.

The solution can be laser microtreatment, which can remove both the polymer matrix and the inorganic filler equally effectively. However, the laser radiation from the most affordable lasers types is nanosecond IR lasers has a significant temperature effect on the processed material. As a result, there is a high risk of material detachment from the substrate due to the difference in CTE of materials. Moreover, the smaller the area of the discrete structure produced with the help of a laser, the greater the probability of detachment.

One of the tasks of RDL composite dielectrics is to approximate the thermal linear expansion parameters of the substrate and the dielectric to each other. In this case, the laser treatment also serves to evaluate the effectiveness of reducing the thermal expansion parameter after adding filler to the dielectric. If the laser exposure to the material did not lead to peeling, it is likely that the resulting structure will withstand other high-temperature processes during the production of RDL.

However, the CTE correlations of the dielectric and the substrate are the most significant, but not the only factor determining the probability of detachment. Different inorganic fillers have different absorption and reflection coefficients of laser radiation. This means that even with the same pulse parameters, the energy absorbed by the material may differ. The distribution of this energy also differs due to the different thermal conductivity of the composite fillers.

As part of this study, it was possible to select a single laser-processing mode for all composites, which ensures the maximum quality of the generated pattern. Manufacturing of microstructures took place on the “MicroSet” IR laser with a wavelength of 1050–1070 nm. The pulse duration parameter was 2 ns, and the pulse frequency was 2000 kHz. The laser pulse power during processing was set to 20 % of the maximum 20 W (0.7 mJ)



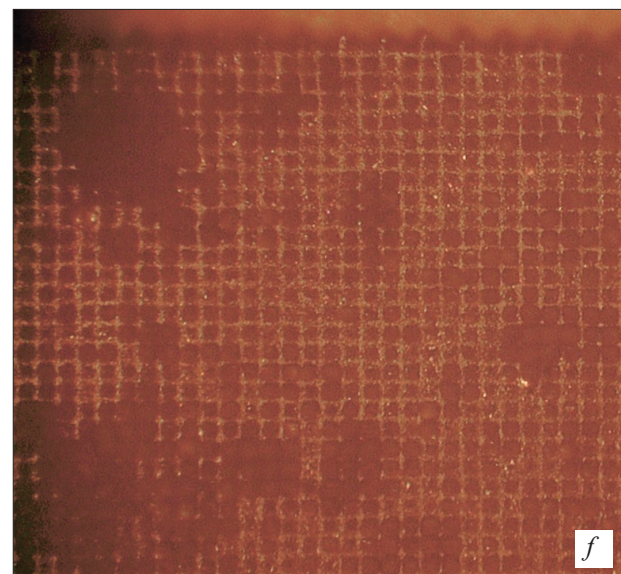
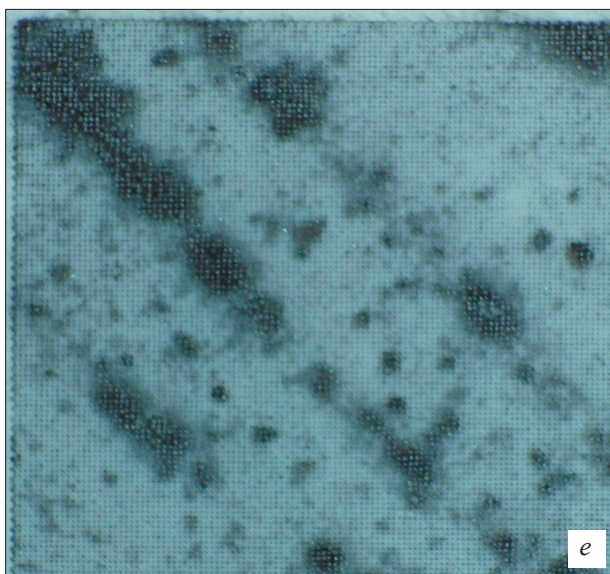
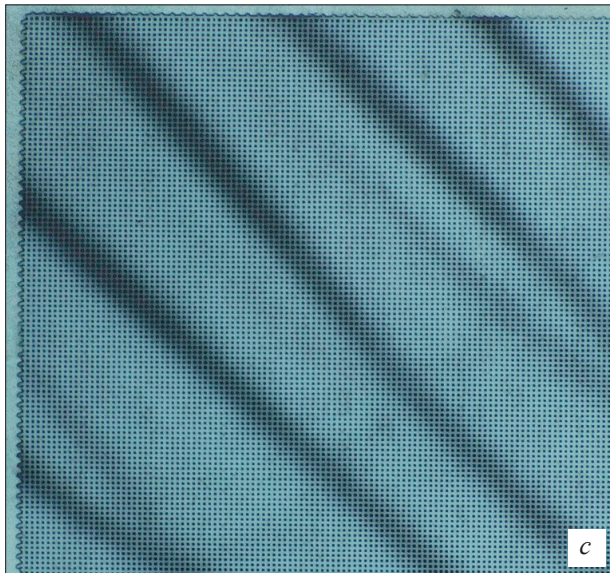
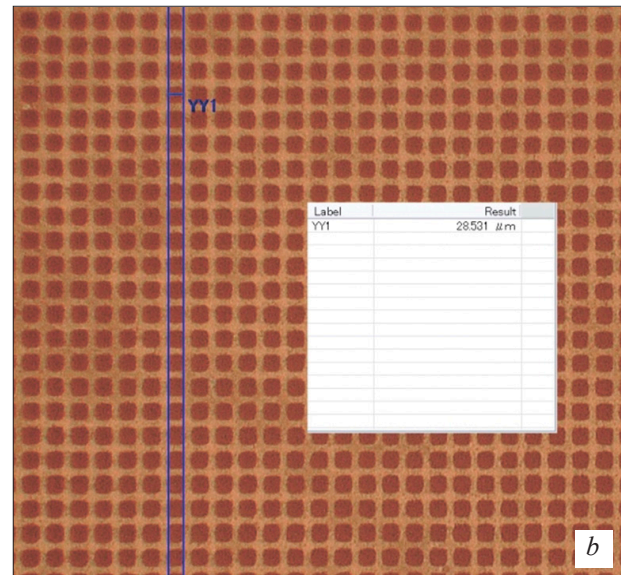
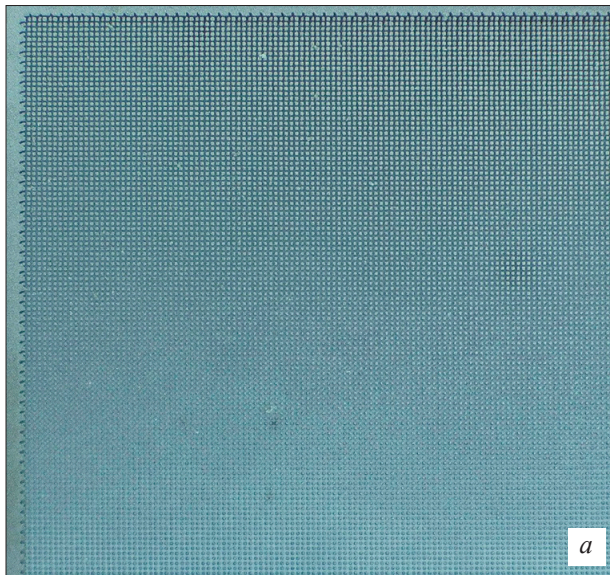


Figure 11. Results of the formation of cylindrical matrix microstructures: composite with cubic boron nitride on glass (*a, b*); composite with technical diamond on sitall (*c, d*), composite with hexagonal boron nitride on sitall (*e, f*)

to prevent the dielectric from charring. The processing speed was 800 mm/s.

Two types of structures were chosen for the formation: the first consists of several tracks of the same length and a gradual decrease in width (from 200 to 50 μm); the second is a matrix consisting of cylindrical elements with a diameter of 30 μm . To form both structures on all types of material, the same pulse duration, frequency and radiation power were used. However, the number of beam passes varied depending on the material. To form these types of structures on a composite with cubic boron nitride, it took one cycle of beam passage, three cycles on a composite with technical diamond, and ten cycles for a composite with hexagonal boron nitride. Presumably, this is due to the uniformity of the applied composite in thickness. After laser exposure, each sample was cleaned in a jet of air with a pressure of 4 atmospheres to remove impurities formed after laser radiation. Figure 10 shows photographs of tracks made on various composites on sital and glass substrates. Figure 11 shows photographs of cylindrical matrix structures made on various composites on sital and glass substrates.

To assess the profile of the obtained structures in height, all samples were additionally examined on the Bruker Contour GT-K optical profiler. Figure 12 shows the results of a study of composite samples with cubic and hexagonal boron nitride on a sital substrate. Figure 13

shows the results of a study of composite samples with copper oxide and technical diamond on a glass substrate.

In terms of the quality and uniformity of the structures obtained, the samples with cubic boron nitride showed the best results. Regardless of the substrate material, this composite had almost no chips on the formed elements, and the uniformity of the geometric shape of the microstructures was observed. None of the tracks and none of the matrix fragments have peeled off, which is evidence of a high level of adhesive strength. The minimum width of the tracks was 52.7 μm , the minimum diameter of the cylindrical elements of the matrix structure was 28.5 μm . The height of the obtained microstructures relative to the substrate ranged from 35 to 45 μm .

Hexagonal boron nitride showed the worst results in both types of structures and on both types of substrates. The tracks have chips and irregularities, and there is no pronounced geometric shape of the formed structures. The profilometric study showed that the resulting structures have a complex relief with large height differences relative to the substrate – from 10 to 50 μm . In the matrix structure, the matrix elements in some areas do not have a clear separation between themselves, in addition, several matrix elements have split off from the substrate. The minimum width of the tracks was 31.3 μm . The diameter of the cylindrical elements of the matrix structure has a high spread – from 30 to 50 μm .

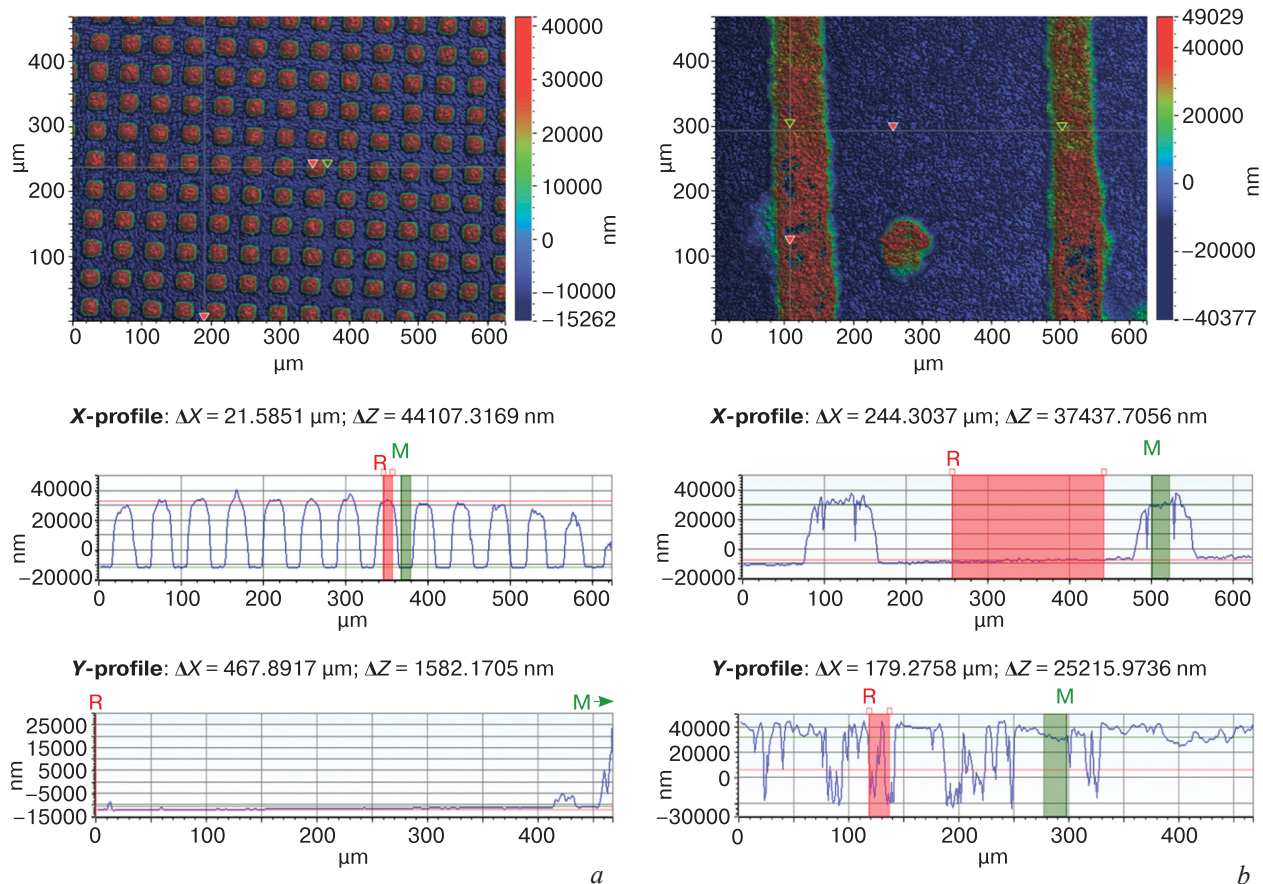


Figure 12. Images of a profilometric study of a composite with cubic boron nitride on a sital substrate (a) and a composite with hexagonal boron nitride on a sital substrate (b)

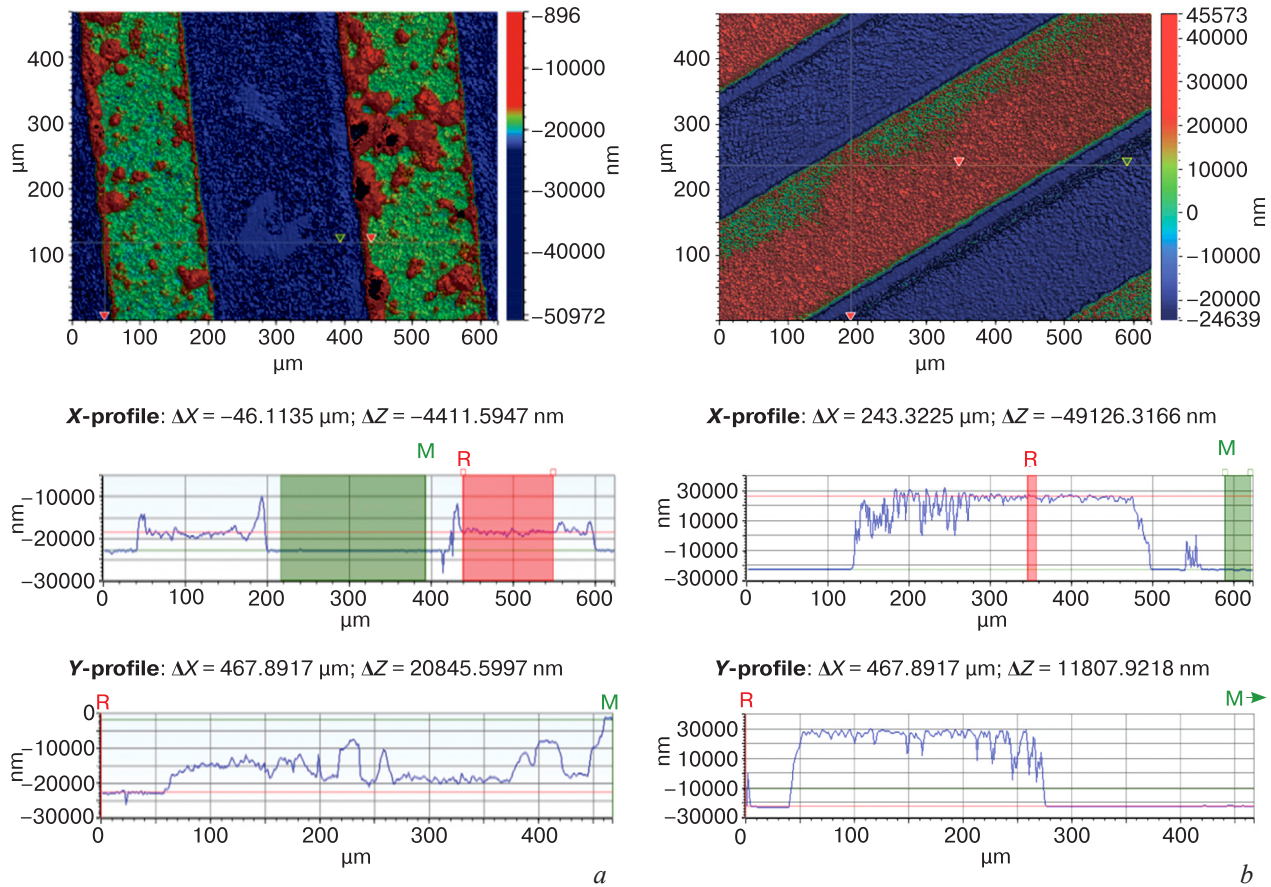


Figure 13. Images of a profilometric study of a composite with copper oxide on a glass substrate (a) and a composite with a technical diamond on a glass substrate (b)

The composite with copper oxide showed similar results to hexagonal boron nitride in terms of the uniformity of the coating in height. The surface of the composite is uneven, with large thickness differences, which can be explained by the heterogeneity of the filler particle size. At the same time, the thickness turned out to be significantly smaller compared to other composites – from 5 to 25 μm . The elements formed on a composite with the addition of copper oxide have clear contours; there are no detachments and large chips. Such a significant difference from a composite based on hexagonal boron nitride, despite the heterogeneity of the surface, can be explained by a higher filling (although CuO particles have different sizes, they are distributed much more evenly in the matrix). Also, this result can be explained by the different nature of the interaction of laser radiation with the composite (different levels of radiation absorption, different thermal conductivity of composites and ablation temperature). The minimum width of the tracks was 30.1 μm . The diameter of the cylindrical elements of the matrix structure is from 30 to 40 μm .

The composite with technical diamond demonstrated results similar to cubic boron nitride, however, there was an uneven size of the microstructures (the diameter of the resulting microstructures varies by one and a half times), which is clearly visible in Fig. 11(c, d), this effect is a consequence of the uneven thickness of the composite layer.

In the darker areas of the matrix structure, the thickness of the composite was greater than in the rest. In addition, Figure 10c clearly shows that the composite was charred after laser treatment. However, it is worth noting that with the same laser ablation modes on a composite with a technical diamond, it was possible to obtain the smallest track width – 28.5 μm , the minimum diameter of the cylindrical elements of the matrix structure was 22.8 μm . The thickness of the composite varies from 30 to 45 μm .

Conclusion

The article describes a study of the adhesive strength of polyimide-based composite materials to siall and glass substrates. Composite materials with fillers in the form of hexagonal boron nitride, cubic boron nitride, technical diamond and copper oxide have been studied. A composite material with cubic boron nitride showed the highest adhesion to both types of substrates – 20.11 MPa on a siall substrate and 20.97 MPa on a glass substrate. Composite with copper oxide showed lowest adhesion on a siall substrate a – 14.78 MPa. Composite based on technical diamond showed minimum adhesion for glass substrate equal 16.74 MPa. When forming microstructures on these composites using an IR laser, it was found that the uniformity of the composite coating on the substrate

has a direct effect on the quality of the resulting microstructures. The composite with hexagonal boron nitride showed the worst quality of tracks and matrix microstructures – there are irregularities in the relief, chips, irregularities in shape and a discrepancy in the geometric dimensions of identical objects. The composite with cubic boron nitride turned out to be the best for microprocessing, in terms of uniformity, distribution and shape of the resulting structures, among the materials studied. The minimum size of the tracks and cylindrical matrix microstructures was obtained on a composite with technical diamond – 28.5 and 22.8 μm . The materials considered in this study can be used as a dielectric in the redistribution layers during the internal assembly of dies, in three-dimensional integration as a dielectric for multilayer side commutation, to create highly integrated substrates on an inorganic base. The successful formation of narrow grooves on the matrix structure opens up the possibility of using such materials for the damascene process, where narrow grooves are formed in the dielectric of the redistribution layer to further fill them with metal and form a topology by removing excess metallization by surface chemical-mechanical polishing.

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Author contributions

Igor A. Belyakov – conducting measurements of composite surface structures using optical profilometry, analyzing experiments results, writing and editing the text of the article; **Mikhail D. Kochergin** – conducting experiments by composites preparing and deposition, taking adhesion measurements using pull-off method, analyzing experiments results, writing the text of the article; **Ilya A. Solovyov** – conducting experiments on the production of cylindrical and linear structures from composites using the IR laser ablation method, analyzing experiments results, writing the text of the article; **Vladimir G. Kurbatov** – conducting granulometric analysis of fillers by laser light scattering and analyzing the results; **Anna A. Gavrilova** – conducting adhesion and composite surface structures measurements, writing the text of the article; **Denis V. Vertyanov** – analyzing experiments results, editing the text of the article.

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