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Formation of submicron relief structures on the surface of sapphire substrates

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An analysis of technologies that allow creating microrelief structures on the surface of sapphire substrates has been carried out. It is shown that the most effective method of forming relief structures with submicron dimensions is ion beam etching through a protective mask formed by photolithography. The main problems in creating a microrelief on the surface of sapphire substrates are the removal of static electric charge in the process of ion beam etching of the substrates, as well as obtaining a protective mask with windows of specified sizes, through which etching of the sapphire substrate is performed.

Keywords: sapphire substrates, selective etching, microrelief structures, protective mask, direct laser recording

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Analysis of the state of the problem

Microrelief structures on the surface of sapphire substrates are widely used in the manufacture of LEDs, diffractive optical elements and long-term data storage media. Most of epitaxial structures for LEDs are grown on profiled sapphire substrates allowing get high efficiency of light output from LEDs. It is known that the profiled substrate scatters the emitted light at the interface of GaN and sapphire and this improves the efficiency of light removal. The efficiency of LEDs grown on profiled sapphire substrates is about 1.5-2 times higher compared to the case of employing the flat sapphire substrates [1-3].

Microrelief diffraction optical elements (DOEs) are formed on sapphire substrates, designed to function at high radiation powers and temperatures [4-6]. To create the microrelief diffraction optical elements on the surface of sapphire substrates, both photolithography methods [4] and the method of laser ablation with femtosecond pulses of ultraviolet radiation are used [5,6]. The micro-profiled sapphire substrates are also proposed to be used to create media for long-term data storage. When creating micro-relief diffraction optical elements on the surface of sapphire substrates and long-term data storage media, special attention should be paid to the formation of elements with submicron strictly defined dimensions. The tolerance for the size of the elements in the horizontal plane should be 30-50 nm, and 20-30 nm in depth. Particularly strict requirements for the size of microrelief elements must be met when manufacturing media with a microrelief structure [7, 8].

The formation of relief on the surface of the sapphire substrate is difficult due to its high chemical resistance. In recent years, several methods of forming a microrelief on the surface of a sapphire substrate have been proposed. These methods of creating a relief on the surface of a sapphire substrate can be divided into two groups. The first one concludes in forming a microrelief in the material of the substrate itself. And the second one provides obtaining a microrelief image in the material applied to the surface of the sapphire substrate. In the first group of methods, the application of chemical etching to create microrelief structures on the surface of sapphire substrates should be highlighted. To profile sapphire one can use etching in a mixture of acids H_2SO_4: H_3PO_4 (H_2SO_4: H_3PO_4 = 3: 1) with employing a mask made of SiO_2 (the temperature of the acid mixture is higher than 300°C). The output pattern on the surface of the SiO_2 layer to be applied to the sapphire is formed either by the method of standard photolithography (to obtain microrelief elements of submicron sizes) or by annealing the deposited nickel layer which leads to the formation of submicron islands that served as a mask during SiO_2 etching [2].

The rate of chemical etching of sapphire is 1 μm/min. [9]. The method of nanosphere lithography can be used to create a microrelief on the surface of sapphire substrates [6]. A mask during sapphire etching can be quasi-ordered hemispherical gold drops of 0.5-3 μm in size, formed in a controlled manner on the surface of sapphire by heating the sputtered solid layer of gold above its melting temperature. The uniqueness of gold as a mask material for this technology should be especially emphasized. Gold is the only metal that combines the necessary chemical resistance with a fairly low melting point. Relief elements have the shape of triangular pyramids. The height of relief elements and their density on the surface can vary significantly depending on the process parameters [1, 2]. Although this method is effective, it is potentially dangerous for the health of operators [9]. To obtain relief structures in the material of sapphire substrates, dry etching in inductively coupled plasma through a mask formed by photolithography is also used [2]. High-frequency ion-chemical etching of sapphire (f_{hf} = 13.56 MHz) was also reported in CF_4 medium (Tetrafluoromethane) [4]. The high chemical resistance of sapphire makes it necessary to apply the dry etching of multilayer masks [9]. One of the layers of the mask is often a layer of metallic chromium, which is necessary to reduce the electrification of the processed sapphire substrate (the specific electrical resistance of sapphire is 10^{19} Ohm cm) [10]., A compensation of the charge on the surface in contact with the plasma is necessary during plasma etching of the sapphire substrates.

To obtain sapphire substrates with regular microrelief on the surface it is suggested to use methods that do not utilize the photolithography technique. Such methods are advisable to apply in the manufacture of diffractive optical elements and optical media for long-term data storage. In one of the options for manufacturing microrelief structures on the surface of sapphire substrates, there is proposed to apply metal to them through stencils with a diameter of holes in the range of 0.2-40 μm by the method of vacuum sputtering and subsequent annealing to form a regular microrelief of sprayed metal on the ultra-smooth surface of sapphire plates [11]. Long-term optical data storage media can be produced by direct laser writing on a layer of photoresist being deposited on a film of chromium on a sapphire substrate [12].

I. The research methods

Ion beam etching of sapphire substrates through windows in organic positive photoresist does not allow obtaining microrelief structures with a depth of more than 70-80 nm. Increasing the etching time leads only to an increase in the size of the elements in the horizontal plane. Such a problem does not arise during ion beam etching of substrates made of silicate glass, on which elements with a depth of 150-200 nm were being formed. The main problems in creating a microrelief on the surface of sapphire substrates are that its etching rate is much lower compared to other materials (for example, silicate and quartz glass). Accordingly, it takes more time to etch sapphire, which leads to a significant accumulation of charge on its surface. Thus, in the process of ion-beam etching of sapphire substrates in order to obtain microrelief structures of given sizes, it is necessary to ensure the avoidance or removal of such surface static electric charge.

To form microrelief structures with submicron dimensions on sapphire substrates by ion beam plasma etching there is proposed to use two-layer masks (conductive layer of chromium and layer of positive photoresist). The masks were being formed by the method of direct laser recording on positive photoresist films and subsequent selective chemical etching of photoresist and chromium layers in various etchants. The scheme of the process on obtaining microrelief structures on the surface of sapphire substrates is demonstrated in Fig. 1.

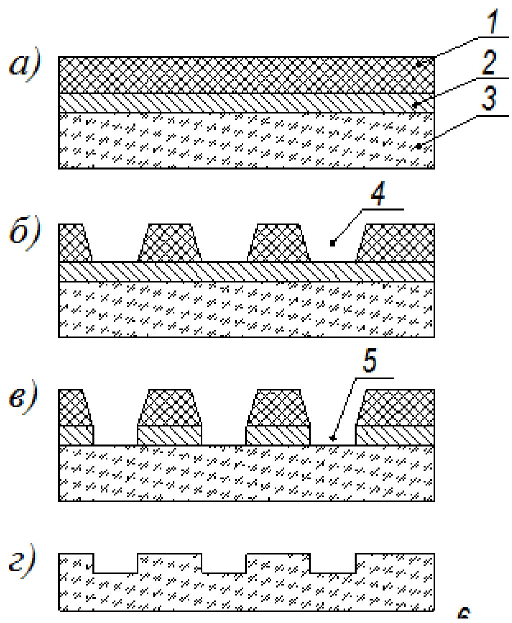

Fig. 1. The process of obtaining microrelief structures on the surface of sapphire substrates: 1- layer of photoresist; 2- chrome layer; 3- substrate; 4- windows in the photoresist; 5 - windows in chrome.

The process of obtaining microrelief structures on the surface of sapphire substrates includes several basic operations:

- direct laser recording on the layer of positive photoresist of the given structure;
- selective etching of the layer of positive photoresist in alkaline etchant;
- selective etching of the chromium layer through the windows in the photoresist layer;
- ion beam etching of the sapphire substrate through a double-layer mask.

The selective chemical etching of the photoresist layer on the surface of the sapphire substrate was carried out with an alkaline etching agent (0.7-1.0% KOH) for 10-20 seconds. The etching time was determined by obtaining the required value of the relative intensity of the diffracted laser beam on the microrelief structure. The selective chemical etching of the chromium layer through the windows formed in the photoresist layer was performed with a standard etching agent based on cerium sulfate and sulfuric acid (cerium sulfate – 200 ml, hydrochloric acid – 100 ml, sulfuric acid – 10 ml, distilled water – up to 1000 ml) [13].

The plasma chemical etching was used to form a microrelief structure in the sapphire substrate. The scheme of the plasma chemical etching installation is presented in Fig. 2.

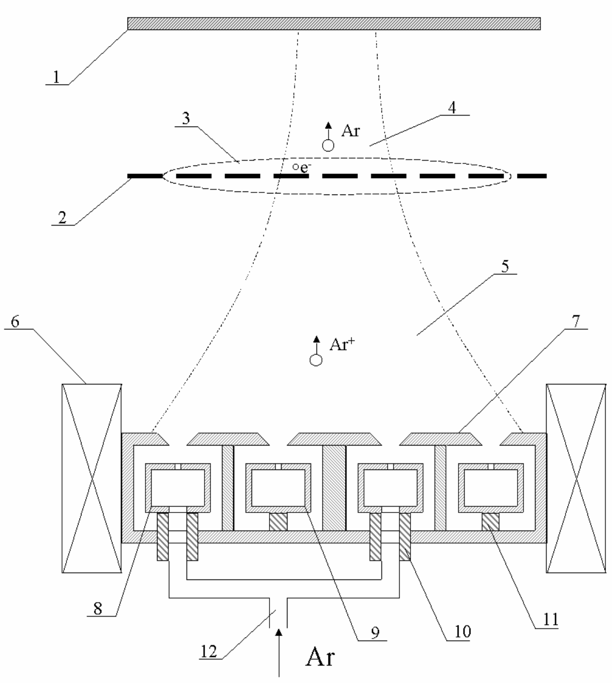

Fig.2. Scheme of the device of plasma chemical etching of sapphire substrates :
1 – work piece; 2 – electron emitter (tungsten filament); 3 – electron cloud; 4 – neutralized ion beam; 5 – ion beam; 6 – focusing coil; 7 – grounded electrode; 8 – alive external gas source; 9 – alive internal gas source; 10 – isolator with gas input; 11 – isolator; 12 – gas input.

The applied technology [14] differs from the known technology of forming microrelief structures in sapphire substrates [4] in that the etching was carried out using a direct current discharge.

II. Experimental studies on the formation of microrelief structures on sapphire substrates

The formation of the image in the layer of positive photoresist was carried out by the method of direct laser recording followed by selective chemical etching in an alkaline solution, and the control of recorded microrelief structures was made with using the analysis of the intensity of the diffracted beam. Fig. 3 shows the image of the surface of disks obtained by the method of direct laser recording on a layer of positive photoresist.

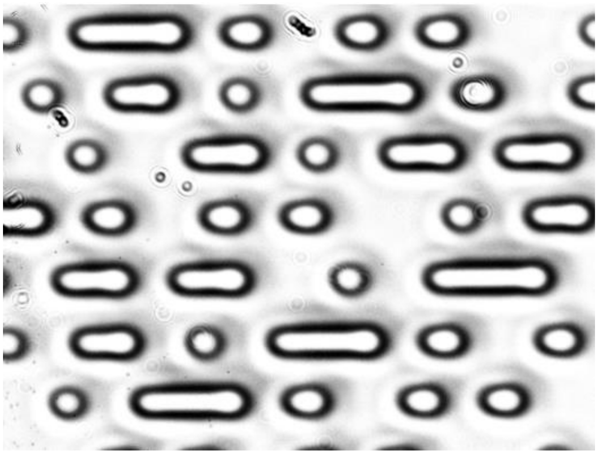

Fig. 3. The disk surface after direct laser recording of submicron structures on the photoresist layer and selective chemical etching of the photoresist.

The deviation of the length of the depressions formed in the process of direct laser recording and selective chemical etching does not exceed 40-50 nm, and the width of the depressions - 100 nm. One of the main problems of obtaining microrelief structures on the surface of sapphire substrates is the presence of a residual layer of positive photoresist in pits formed after recording and selective chemical etching of the photoresist layer with an alkaline etching agent. As our experiments have shown, the formation of microrelief structures of a given depth is strongly influenced by photoresist residues in micro-holes (pits), through which the chrome layer is etched. Increasing the time of selective etching of the chromium layer on samples with remnants of photoresist in the micro-holes does not allow obtain the recess of the required uniform depth. Etching in an ultrasonic field helps to the uniform chromium etching [15].

The use of ultrasound-assisted etching requires the use of substrates with minimal mechanical stresses. The presence of micro-cracks and significant mechanical stress leads to the destruction of the substrate in the process of ultrasonic treatment. Fig. 4 demonstrates the image of the surface of the sapphire substrate after selective etching of the chromium layer through the windows in the photoresist layer with remnants of the photoresist in the micro-holes.

The effect of incomplete removal of the photoresist is the reason for the distortion of the micro-relief structure and the formation of micro-holes with a stepped shape and different depths. The incomplete removal of the photoresist in the micro-holes is associated with insufficient exposure of the samples and a local change in the properties of the photoresist layer after exposure. The appearance of a residual layer of positive photoresist was observed during laser recording of ring chromium templates and is associated with the fact that due to the relatively high transparency of the photoresist layer.

Thus, a significant portion of the energy of the recording laser beam is absorbed by the chromium film under the photoresist. This leads to heating of the chrome film and, accordingly to a decrease in the sensitivity of the photoresist. As a result, the photoresist film may be underexposed near the chrome-photoresist border. As a result, a thin residual layer of acid-resistant positive photoresist is formed on the bottom of the microelements, which prevents the etching of chromium by acid etching. The effect of the residual layer of photoresist on the bottom of the microelements on the etching process of the chromium layer can be almost completely eliminated by optimizing the concentration of the etching agent. Experiments have shown that for selective etching of elements recorded on a photoresist film with a thickness of 0.5 μm applied to a chromium film, the optimal concentration of KOH should be 1% [16]. To avoid the formation of a residual layer of photoresist on the bottom of the microelements, we also increased the concentration of KOH to 1%. This made it possible to carry out more homogeneous etching of chromium through the windows in the positive photoresist. Further selective chemical etching of the chromium layer made it possible to obtain a two-layer mask through which etching of the sapphire substrate was carried out (Fig. 5).

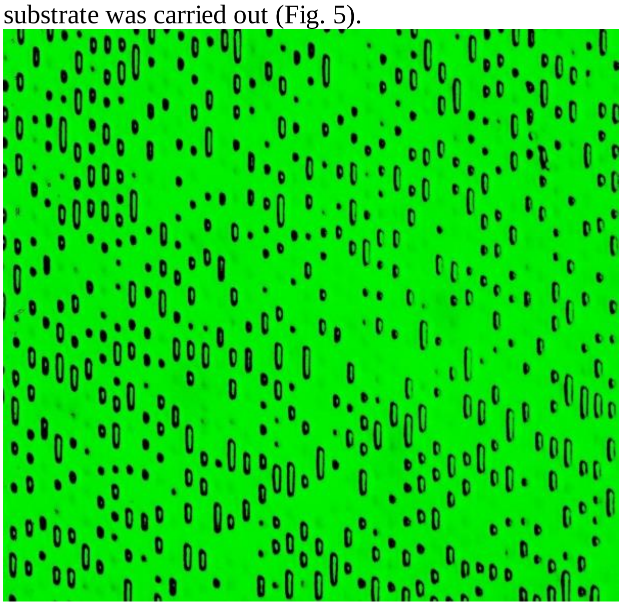

Fig.4. The surface of the sapphire substrate after selective etching of the chromium layer through the windows in the photoresist layer with photoresist remnants in the micro-holes.

Extraction of electric charge from the surface of the sapphire substrate during its plasma chemical etching was performed by grounding the metal layer of the protective mask using conductive paste. The compensation of the electric charge on the surface of the sapphire substrate made it possible to form relief structures with a depth of 120-200 nm by plasma chemical etching through a two-layer protective mask. The thickness of them was 160 nm of a layer of positive photoresist Shipley 1813 and a 30 nm layer of chromium. The plasma chemical etching of sapphire substrate through a two-layer protective mask was made in the following modes: residual pressure in the vacuum chamber- $2*10^{-2}$ Pa; the operating pressure of the Freon(CF_4) - $4*10^{-2}$ Pa; etching time -12.5 minutes; the current of ion beam - 1A; accelerating voltage - 2.2 kV; the lens current –76 mA; the angular speed of the carousel with substrates - 20 rpm. Fig. 6 shows the image of sapphire substrates after the plasma chemical etching through a two-layer mask - the layers of positive photoresist and chromium.

Fig. 5. The disk surface after chemical etching of the chrome layer (image of a two-layer mask on the surface of the sapphire substrate).

Fig. 6. Optical image of the surface of sapphire substrate after plasma chemical etching through a two-layer mask: a layer of positive photoresist and a layer of chromium (obtained with use of NEOPHOT 2).

Fig. 7 demonstrates the images of ASM from the surface of the sapphire substrate after plasma chemical etching. It shows that the depth of the microrelief structure is 157 nm.

After the plasma-chemical etching process was completed the double-layer mask was stored on the surface of the sapphire substrate which made it possible to obtain microrelief structures of greater depth.

Conclusions

1. The formation of submicron relief structures on the surface of sapphire substrates is an urgent problem. A significant number of technologies are proposed to solve them. In most of the proposed technical solutions, the use of multi-layer protective masks is proposed.

2. One of the main problems during the creation of a regular microrelief on the surface of sapphire substrates is the obtaining of a protective mask through which etching

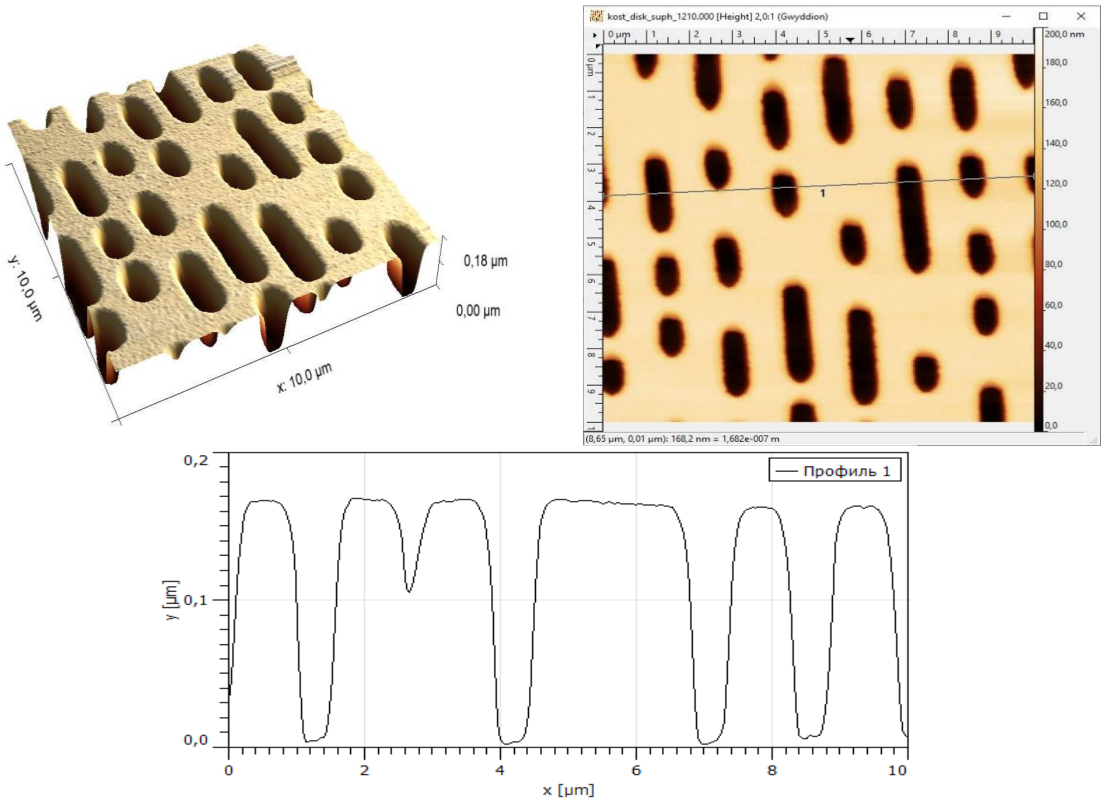

Fig.7. ASM image of the sapphire disk after the plasma-chemical etching (the pit depth is 159 nm).

of the sapphire substrate is being carried out. Deviations from the specified shape of the holes in the protective mask affect the quality of the micro-relief structure of the sapphire substrate.

3. The most promising and technological method of creating a regular microrelief on the surface of sapphire substrates is plasma chemical etching of sapphire substrates through windows in multilayer protective masks.

4. An alternative method for micro profiling of sapphire substrates is the technology of microrelief formation in an additional layer applied to the surface of the sapphire substrate. This technology can be considered promising for the creation of long-term data storage media.

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Формування субмікронних рельєфних структур на поверхні сапфірових підкладок

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Проведено аналіз технологій, які дозволяють створювати мікрорельєфні структури на поверхні сапфірових підкладок. Показано, що найбільш ефективним методом формування рельєфних структур із субмікронними розмірами є йонно-променеве травлення через сформовану методом фотолітографії захисну маску. Основні проблеми при створенні мікрорельєфу на поверхні сапфірових підкладок полягають у видаленні статичного електричного заряду в процесі йонно-променевого травлення підкладок, а також отриманні захисної маски з вікнами заданих розмірів, через яку здійснюється травлення сапфірової підкладки.

Ключові слова: сапфирові підкладки, селективне травлення, мікрорельєфні структури, захисна маска, прямий лазерний запис.