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REMOVAL OF PHOTORESIST MASKS WITH THE USE OF RAPID HEAT TREATMENT

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An analysis of the main methods of removal of photoresists, used in microelectronics, has been performed. The possibility of using rapid heat treatment for this purpose has been investigated and results of an analysis of the surface of silicon and aluminum after the removal of a photoresist have been presented. All the results have been considered in comparison to the traditional methods of removal of a photoresist, used in the technology of manufacture of very large-scale integrated circuits.

Chemical, physicochemical, and physical methods of removal of a photoresist are used at present in the process of manufacture of very large-scale integrated circuits. The main techniques used in this case are either the treatment of the photoresist in corresponding solvents or complex treatment with the use of oxidizers.

Films of positive photoresists are easily removed by ordinary dissolution in acetone, dioxane, dimethyl formamide, or aqueous-alkaline solutions. However, if the etching is preceded by a thermal treatment sufficient for thermolysis, the procedure of removal of a photoresist becomes much more complicated and requires the use of oxidizers or mechanical action. An example is the widely accepted procedure of removal of a photoresist with the use of organic solvents (mixtures of dimethyl formamide and monoethanolamine) and application of an ultrasonic field in certain cases, for example, in the formation of plating. However, the use of chemical treatment in combination with the mechanical action by an ultrasonic field does not always make it possible to remove the photoresist completely.

Positive photoresists that had a drying temperature of lower than $110^{o}C$ prior to the etching are easily removed from the surface of a plate in weak-alkaline solutions if the photoresist was irradiated with ultraviolet light prior to the treatment.

Because of the long time and high temperatures of treatment of positive photoresist films, pure oxidizers or a mixture of solvents with an oxidizer and a peroxidic-ammonia solution are required for their removal. The action of oxidizing reagents destroys photoresist films. However, their use is limited by the possible corrosion of the substrate material. The corrosion action of such compositions increases if two metals of a circuit with different electrochemical potentials are in contact. Despite this fact, this method is widely used at present. Caro's acid (mixture of equal parts of concentrated sulfuric acid and 30% hydrogen peroxide) is used for substrates that can stand up to the action of an oxidizer. The photoresist is removed at a temperature of $100^{o}C$ in Caro's peroxomonosulfuric acid, which oxidizes and destroys the photoresist film, transforming it to solution [1].

To increase the efficiency of removal of a photoresist and the time of action of Caro's peroxomonosulfuric acid, a concentrated sulfuric acid is heated to $60^{o}C$ prior to its mixing with hydrogen peroxide. This leads one to the necessity of using a higher temperature ($150^{o}C$) to remove the photoresist. However, these measures give no way of obviating a significant limitation of the method — the efficiency of removal of the photoresist sharply decreases with decomposition of Caro's acid. Furthermore, this method is characterized by the high specific consumption of materials and has a harmful effect on the environment.

There is a method of removal of a photoresist which is based on the use of peroxide-ammonia solutions for this purpose. However, it does not provide the necessary cleanness of the surface, since photoresist cannot be removed for a small concentration of ammonia and the oxidizing processes are not sufficiently powerful because of the rapid decomposition of hydrogen peroxide. If we treat a surface from which photoresist has been removed by the plasma

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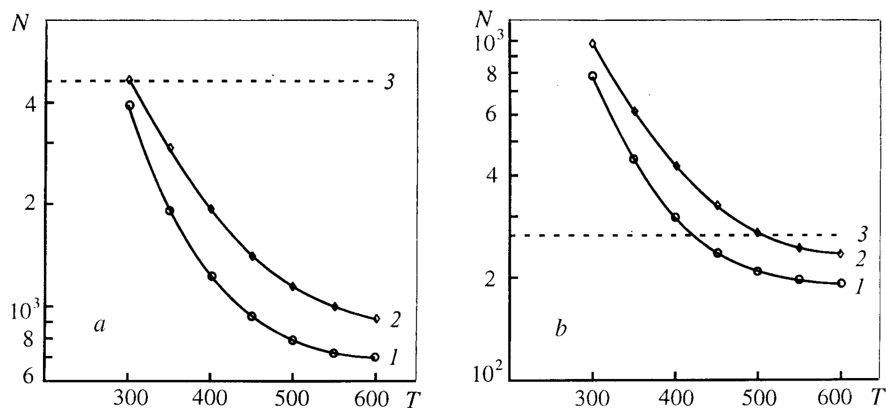

Fig. 1. Dependence of the density of light-emitting points (a) and ash residues (b) after the removal of a photoresist with the use of RHT by pulses of second (1) and millisecond (2) duration on the temperature of treatment; 3) density of defects after the standard method of removal of a photoresist. *N*, cm^{-2}; *T*, ^oC.

chemical method in a peroxide-ammonia solution, analysis of it by the method of Auger spectroscopy will reveal a high content of carbon on it.

In the Lourier method, a photoresist is removed with a mixture of monoethanolamine and hydrogen peroxide. However, this method has the same limitations as in the case of using Caro's acid for this purpose.

At present, a solution of ammonium nitrate in a concentrated sulfuric acid is widely used for removal of a photoresist from metal-free substrates.

Along with chemical methods one widely uses plasma-chemical methods of removal of a photoresist, which are dependent on the preliminary treatment to a much lesser extent than the above-indicated methods. The plasma-chemical method of removal of a photoresist is based on the interaction of oxygen with the photoresist with the resulting formation of carbon dioxide, water, and other volatile oxides. However, this method is not sufficiently powerful in the case where it is used after the implantation of boron, phosphorus, antimony, and other ions in large doses and for high energies. In this case, ash residues are left on the plates. They represent complex involatile polymeric compounds that are not removed even in the case where the time of treatment in the plasma is increased three times. This is explained by the fact that masking photoresist layers acquire new properties (not characteristic of them in the usual state) after ion-implantation doping: their mechanical and chemical stability increase, the transparency deteriorates, etc. Therefore, the ash residues of the photoresist on the plates from which the photoresist has been removed by the plasma-chemical method can be considered as involatile organic compounds with very strong chemical bonds formed as a result of the decomposition of the polymers.

Analysis of the main methods of removal of a photoresist used in microelectronics shows that at present there is no universal method for conducting this operation. In this connection, it is of interest to consider the possibility of using rapid heat treatment (RHT) for this purpose.

To evaluate the quality of the surface of silicon and aluminum after the removal of a photoresist by the RHT method and the method of plasma-chemical etching followed by chemical treatment (standard treatment), we determined the density of light-emitting points and ash residues in the dark field of a microscope. In addition, we performed a comparative analysis of the quality of the surface of silicon and aluminum by the method of Auger spectroscopy. In the case where the RHT method was used for removal of the photoresist, the back surface of the plates was exposed to the radiation of xenon lamps with a pulse duration of 50 msec for an energy density from 60 to 120 J/cm^2 and to the radiation of halogen lamps with a pulse duration from 1.4 to 8 for a power density of 35 W/cm^2. This provided heating of the silicon plates from 400 to 1200^oC.

The investigations have shown (Fig. 1) that the density of the light-emitting points after the rapid heat treatment by the pulses of millisecond and second duration is almost an order of magnitude lower than that after the standard treatment and the amount of ash residues on the surface of the substrate in the first case is two times smaller than that in the second case. This means that in the case of rapid heat treatment, the sublimation of the photoresist provides

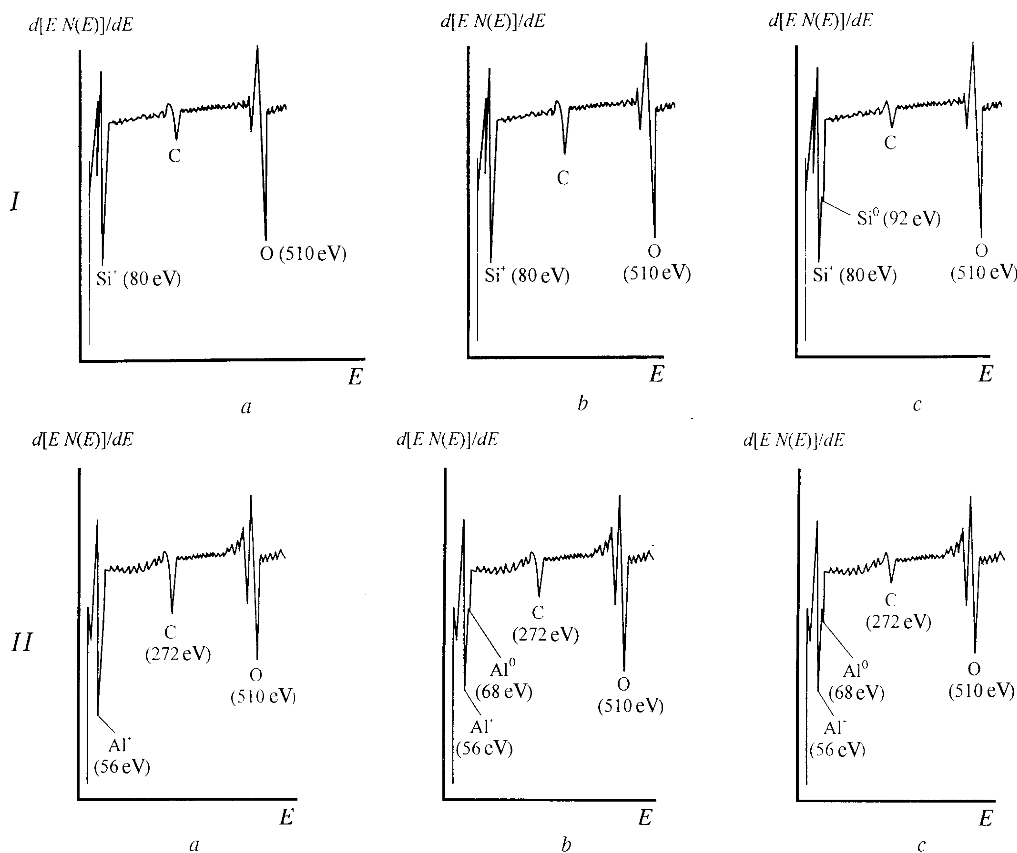

Fig. 2. Auger spectra of the surface of silicon (I) and aluminum (II) after the removal of a photoresist by the standard method (a) and with the use of RHT by pulses of millisecond (b) and second duration (c). *E*, eV.

a more complete removal of it from the surface of the plates than in the case of standard treatment. Furthermore, such heating leads to the removal of inorganic contaminants, such as deposited specks of dust or other defects, which burn up at such high temperatures. In this case, the best results are obtained when the surfaces are treated by pulses of second duration, because the effective time of heating with such pulse durations is longer than that in the case where pulses of millisecond duration are used.

A comparative analysis of the Auger spectra of the surfaces of silicon and aluminum from which the photoresist has been removed by the RHT method and the standard method was performed by the ratio between the Auger peaks of the main atomic components Si^0, Al^0, Si^+, Al^+, C, and O (to the atomically pure elements Al and Si there corresponds the notation Si^0 and Al^0 and to the bound state there corresponds the notation Si^+ and Al^+) (Fig. 2). Our investigations have shown that the efficiency of removal of the photoresist by the RHT method depends on both the initial state of the surface treated and the regimes of the RHT process. In the case of removal of the photoresist by rapid heat treatment, the peak of C is smaller than in the case of plasma-chemical removal of the photoresist followed by chemical treatment, which points to the effective sublimation of organic contaminants from the surface treated. In this case, this peak decreases more markedly when the treatment is performed by pulses of second duration because of the longer time of their action on the surface. The appearance of the peaks of Si^0 and Al^0, which have a larger value in the case of treatment by pulses of second duration, points to a decrease in the bound states and an increase in the free states on the surface after the rapid heat treatment. Furthermore, there is a small change in the peak of O, which is apparently due to the decrease in the concentration of the OH group on the surface of the film and the removal of moisture from it. This confirms the fact that the thickness of an Al_2O_3 film on aluminum, as the ellipsometric measurements have shown, is independent of the method of removal of the photoresist and it remains constant. At the same time, high-temperature heating in the case of rapid heat treatment causes both evaporation of moisture from the surface of the film and breaking of the bonds of the OH group with aluminum, which leads to an increase in the free states

and causes the appearance of peaks of Si^0 and Al^0. This process is particularly advantageous in removal of moisture and the OH group from the intergranular boundaries, which are difficult to remove in the case of chemical treatment because of the difficulty of penetration of chemical reagents there.

Thus, rapid heat treatment by pulses of millisecond and second duration can successfully be used for removal of a photoresist from the surface of various materials, which provides a higher quality of cleaning of the surface than plasma-chemical cleaning followed by chemical treatment. In this case, the efficiency of treatment by pulses of second duration is higher because the time of heating of samples is much longer in this case than in the case where pulses of millisecond duration are used.

NOTATION

T, temperature, ^{o}C; N, density of defects, cm^{-2}; E, energy of electrons, eV; $d[EN(E)]/dE$, relative units.

REFERENCES

1. V. P. Lavrishchev (ed.), *Introduction to Photolithography* [in Russian], Moscow (1977).