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Surface Morphology of Silicon Single Crystals Treated with Acid Polishing Etchants[1]

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Abstract—The specific features of formation of micro- and nanorelief on the (001) surface of silicon single crystals upon treatment with widely used etchants HF–HNO_3–H_2O and with poorly studied etchants HF–$KMnO_4$–H_2O were studied. The relief of the etched surface was examined by optical, scanning electron, and atomic-force microscopy. The polishing properties of the etchants and the silicon etching rates were studied in relation to the oxidant content. The polishing properties of the etchants were compared by analyzing statistical distribution of such characteristics of the relief of the etched surface as the height and length of micro- and nanowaves.

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Growing attention is given today to the physical and chemical properties of the surface of single-crystalline silicon, the main material of modern electronics and a promising material for the electronics, optics, mechanics, and analytical chemistry of the future. These properties determine not only the principle of functioning of micro- and nanodevices, but also their manufacturing procedure. The solution of many technological problems is associated with the ability to form the required type of the micro- and nanorelief of the single crystal surface. In particular, in view of the tendency toward miniaturization of silicon devices for various purposes, preparation of nanosmooth and atomically smooth surfaces becomes an important problem of modern silicon technology. One of methods allowing solution of such problems is liquid chemical etching. Acid etching allows the surface reconstruction to be performed at ultimately low temperatures, and only under these conditions it is possible to obtain atomically smooth surfaces and to form nanoobjects ordered with an atomic accuracy [1]. However, physical and chemical aspects of etching of perfect single crystals of silicon in acid solutions have been studied inadequately, despite wide use of this process in microelectronics technology, with empirically chosen conditions for various steps of production of modern semiconductor devices. The existing kinematic and molecular theories of dissolution of single crystals describe this process insufficiently adequately. The results of experimental studies of dissolution of silicon single crystals are contradictory and difficultly reproducible in detail [2].

Here we report on a comparative study of specific features of the relief of the (001) surface of silicon single crystals upon etching in widely used solutions HF–HNO_3–H_2O (in the range extended toward low HNO_3 concentrations) and in poorly studied etchants, HF–$KMnO_4$–H_2O.

HF–HNO_3–H_2O Etchants (I)

Etching rate. In experiments with etchants I under the above-indicated conditions, we determined the dependence of the dissolution rate of the (001) surface of single-crystalline silicon on the HNO_3 content (including the region of its low concentrations, which was not examined previously). The shape of the dependence obtained (Fig. 1) is consistent with the previous data [2]. The maximum of the etching rate is observed at HNO_3 concentrations of 3–4 M. An increase in the dissolution rate with an increase in the oxidant concentration from 0.17 M is determined by the rate of silicon oxide formation, and the subsequent decrease in the reaction rate with an increase in [HNO_3] to 11.0 M is due to formation of poorly soluble reaction products preventing the diffusion of the complexing agent to the reaction surface.

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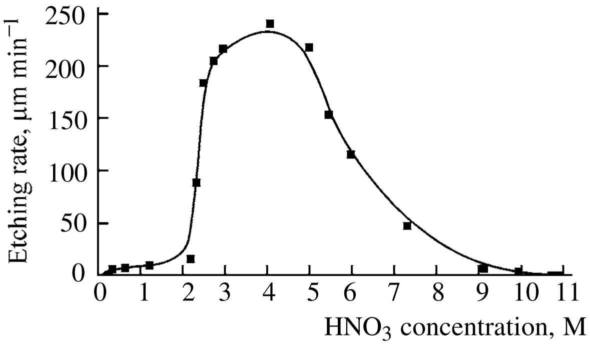

Fig. 1. Etching rate of the (001) surface of silicon single crystals in $HF–HNO_3–H_2O$ solutions at 20°C as a function of the HNO_3 concentration.

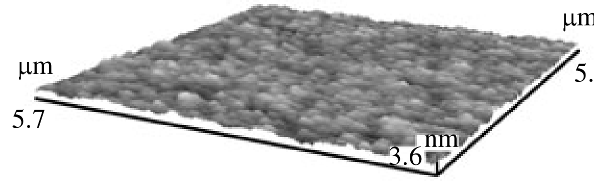

Fig. 2. Topography of the (001) surface of single-crystalline silicon after etching in $HF–HNO_3–H_2O$ (10.9 M HNO_3) to a depth of 1 μm (AFM pattern).

Surface morphology. An example of the relief formed by etching of the silicon surface in etchants I is shown in Fig. 2. It is seen that the relief consists of waves of different lengths and heights. Analysis of the statistical distribution of these parameters shows that the wave height increases with a decrease in the HNO_3 concentration in etchants I (Fig. 3). For example. at [HNO_3] 11.0 M the prevalent wave height is 1.5 nm, and at [HNO_3] 9.1 M, 4.5 nm (the prevalent height of waves on the surface of the initial samples is 9 nm).

This dependence of the relief of the etched surface on the HNO_3 concentration is due to a change in the dissolution mechanism in the examined range of HNO_3 concentrations. At low HNO_3 concentrations, the autocatalytic oxidation with HNO_2 as catalyst is the rate-determining step. In the process, as a rule, the surface becomes rougher. At high HNO_3 concentrations, the dissolution becomes diffusion-controlled, which results in formation of a smooth surface [3].

Our results show that etchant compositions providing formation of the smoothest relief of the (001) surface of silicon single crystals correspond to the upper limit of the examined range of HNO_3 concentrations.

$HF–KMnO_4–H_2O$ Etchants (II)

Etching rate. When studying a series of $HF–KMnO_4–H_2O$ solutions, we observed an increase in the etching rate with an increase in the oxidant concentration (Fig. 4).

The linear dependence of the etching rate on the oxidant content indicates that the dissolution kinetics

(a) (b)

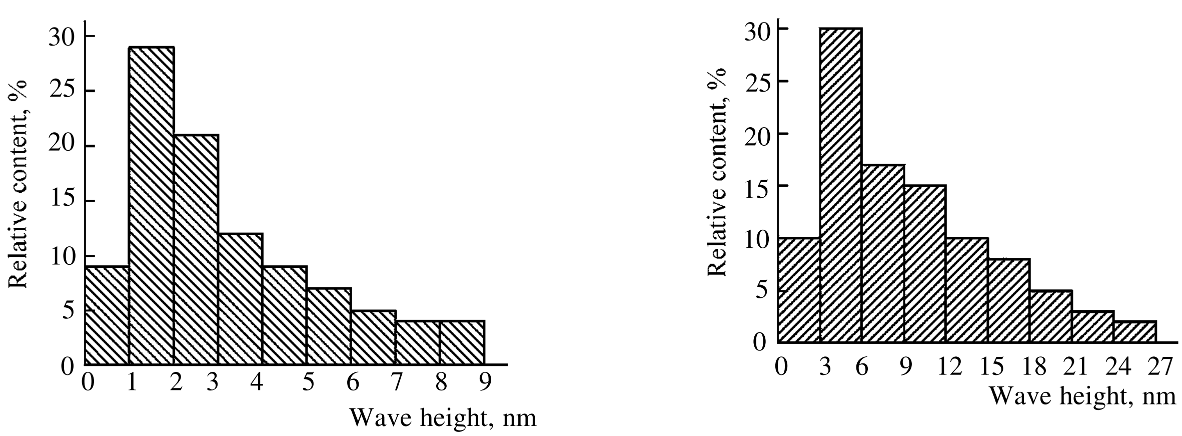

Fig. 3. Distribution of wave heights on the etched surface at HNO_3 concentrations of (a) 10.9 and (b) 9.1 M (etching depth 1 μm).

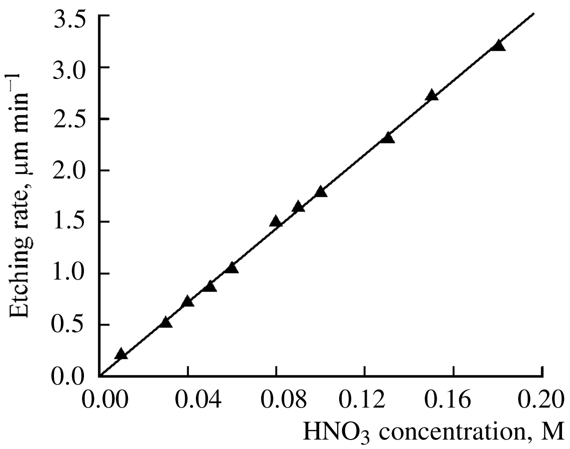

Fig. 4. Etching rate of the (001) surface of silicon single crystals in $HF–KMnO_4–H_2O$ solutions at 20°C as a function of the $KMnO_4$ concentration.

is controlled by the same process throughout the examined range of $KMnO_4$ concentrations. This process is presumably diffusion of the reaction component. This conclusion also follows from the dependence of the height of the surface relief on the oxidant concentration in etchants II (Fig. 5).

Surface morphology. Analysis of the statistical distribution of the heights and lengths of waves formed by dissolution of the silicon surface in etchants II shows that the wave height increases with an increase in the $KMnO_4$ concentration (Fig. 5). For example, at the oxidant concentration of 0.01 M the prevalent wave height is 0.2 nm, and at its concentration of 0.1 M, 1.4 nm.

Our results show that etchants with the minimal oxidant content are characterized by the best polishing properties.

Comparison of Etchants I and II

Comparison of the polishing properties of the best etchants among those we studied shows that etchants II provide formation of a smoother relief than etchants I (Figs. 3a, 5a, 6). This difference in the effect of etchants with different oxidants is due to the greater significance of the diffusion constituent in the set of surface reactions of silicon dissolution in etchants II. We intend to study in more detail the features of dissolution of single-crystalline silicon surfaces with various crystallographic orientations in etchants of different compositions.

EXPERIMENTAL

Specimens (5×5 mm^2) with the (001) surface orientation were prepared from dislocation-free single-crystalline p-type silicon wafers with a resistivity of 4.5 Ω cm. The single crystals were grown by the Czochralski technique. The polishing properties of $HF–HNO_3–H_2O$ (etchants I) and $HF–KMnO_4–H_2O$ (etchants II) solutions were studied in relation to the oxidant content. The concentration range examined was as follows: HNO_3 0.17–11.0 and $KMnO_4$ 0.01–0.18 M (HF 28.0 M). The choice of these concentration ranges was governed by the following factors. At HNO_3 concentrations below the lower limit of the indicated range, a nonuniform relief is formed at a low dissolution rate, because of the kinetic control of the surface reactions of silicon dissolution (autocata-

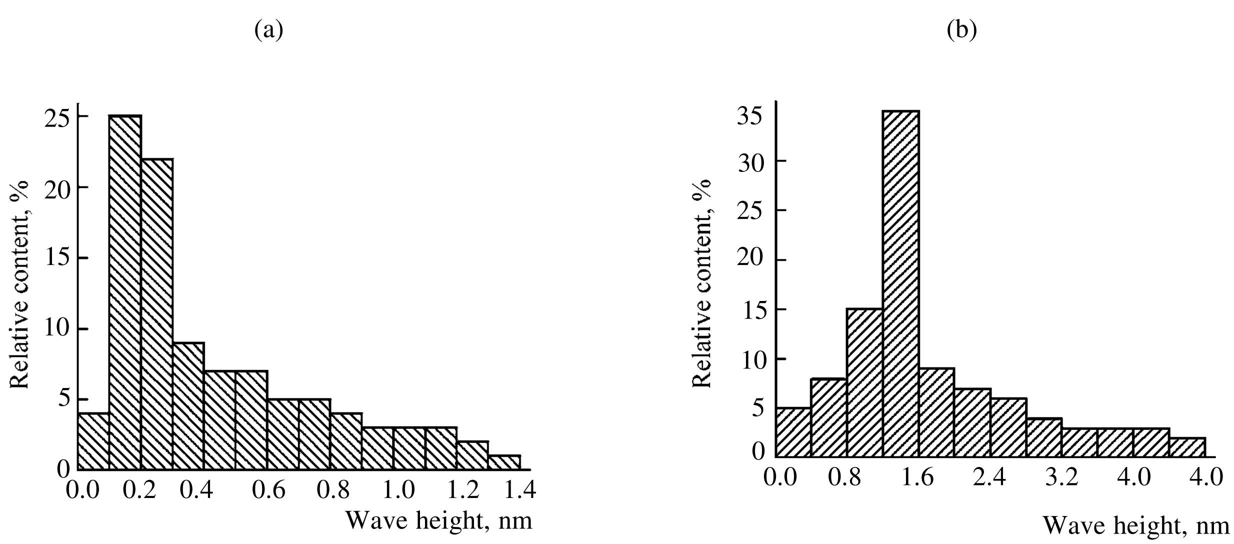

Fig. 5. Distribution of wave heights on the etched surface at $KMnO_4$ concentrations of (a) 0.01 and (b) 0.10 M (etching depth 10 μm).

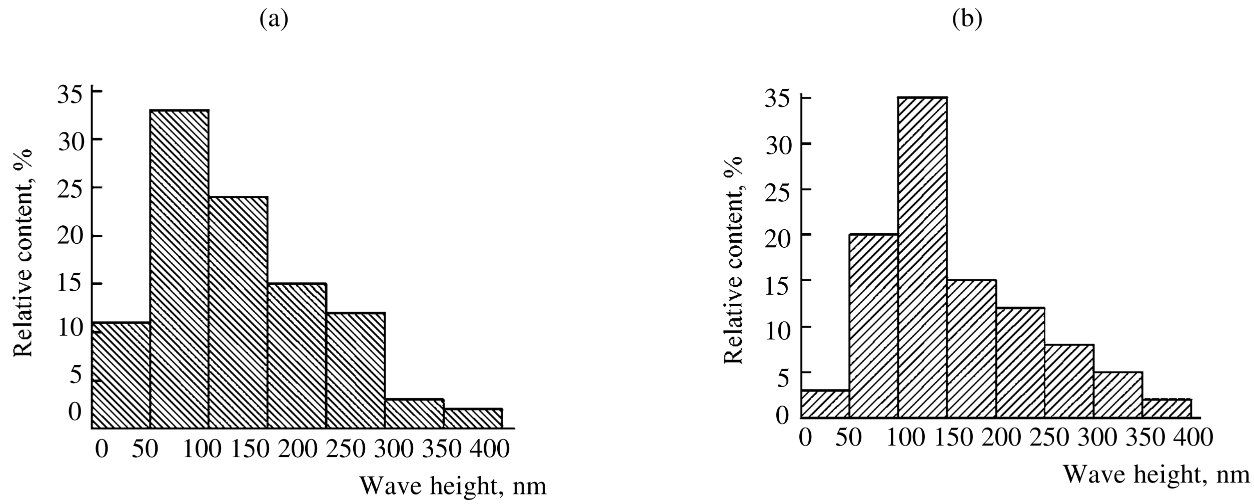

Fig. 6. Distribution of wave lengths on the (001) surface of silicon single crystals treated in following solutions: (a) etchant II (0.01 M $KMnO_4$, etching depth 10 μm) and (b) etchant I (10.9 M HNO_3, etching depth 1 μm).

lytic oxidation limits the dissolution rate). At HNO_3 concentrations above the upper limit, insoluble oxidation products formed. At $KMnO_4$ concentrations below the lower limit, the dissolution was hindered by formation of unidentified insoluble products, and this phenomenon requires a more detailed study. The upper limit of the $KMnO_4$ concentrations is determined by its solubility under the experimental conditions.

The dissolution was performed in a Teflon vessel at 20°C with continuous stirring. The morphology of the etched surface was examined with an MII-4 interference microscope, an LEO-1420 scanning electron microscope, and an NT-206 atomic-force microscope. The polishing properties of the solutions were compared by analyzing the statistical distribution of the size of the relief components (height and length of micro- and nanowaves) on the etched surface.

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