Investigation of the effect of technological parameters on efficiency of chemical string cutting of semiconductor materials

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Abstract. On the basis of the balance model for convection-diffusion processes that occur during string chemical cutting (CC) of samples, we derive an analytical expression for the limiting CC rate at maximal use of etching agent. Comparison between the experimental and theoretical dependencies of CC rates for InSb, HgCdTe and CdTe samples on the velocity of string motion and diameter of sample being cut demonstrates good agreement of the experimental results with the model notions. It is shown that diffusion kinetics of the CC process is retained even at very high velocities of string motion. The experimentally obtained value of CC rate is approaching 3 mm/min. The dependencies studied point at resources for increase of CC efficiency. Some technical modification of the equipment, related primarily to increasing velocity of motion of the etching liquid carrier, will make the CC technique able to meet competition with the abrasion techniques in technological lines for manufacturing of semiconductor devices.

Keywords: chemical cutting, string chemical cutting, string.

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1. Introduction

Appearance of the chemical cutting (CC) technique was dictated by the need for production, in an effort to study, of thin cuts of structurally-sensitive materials (initially metal single-crystals) without introduction of structural defects into them [1]. In this technique sample separation from ingot occurs due to local chemical solution of the ingot material near the etchant-carrying “cutting” tool, without mechanical contact between the tool and ingot. So near-surface layers in the samples prepared using the CC technique retain structural perfection of the starting ingot material.

Application of the CC technique rather than the conventional abrasion ones in the semiconductor device manufacturing technology could save high-cost material and make products of higher quality than when using the abrasion processing techniques. At present, however, operating efficiency of the CC technique is substantially below that of the abrasion techniques. This is one of the factors that prevent wide industrial application of the CC technique. So there exists practical need for revealing and analysis of the principal factors that determine operating efficiency of the CC technique, in an effort to find possibilities and resources for its increase.

2. Model

In conventional CC facilities a chemically active liquid is usually carried to the sample being cut with a moving string to which an etchant adheres. When the carried agent comes into contact with the sample, then chemical interaction occurs between them. As a result, a void appears in the sample. The reaction products that are generated in the cutting area are removed from it by the same moving carrier. If etchant input into the cutting area, removal of reaction products out of it and sample feed to the carrier are coordinated, then a cut surface is formed.

The operating efficiency of the above process depends on a number of parameters, such as the velocity of carrier motion, initial etchant concentration, sample size, etc. A rigorous analysis of their effect on the operating efficiency makes a rather complicated problem. So it seems reasonable to start from consideration of a simplified model for the process. For definiteness sake, let agent carrier be a string whose diameter is much over a gap between the string and the sample being cut. This assumption enables one to take the string surface as being flat.

Let the sample length is $l$, and the chemical agent solution fills the whole space between the string and sample. The string is moving with a constant velocity $u$ and is
dragging an etchant layer (whose thickness is \( \delta \)). A stationary agent layer (whose thickness is \( \delta \)) is next to the sample surface (that is initially flat). The agent molecules diffuse to the sample surface and come into contact with its material. The result of the reaction is chemical dissolving of the sample. The length of the gap between the string and sample (that is equal to the sample length) is much (by several orders of magnitude) over the gap width. Therefore one can consider diffusion in the gap as being transverse only.

In the course of cutting solution in the gap is depleting. So the agent concentration \( c \) at the reaction surface decreases along the direction of string motion. Accordingly, the sample dissolution rate is to decrease along this direction. Distinction between the dissolution rate values at different reaction surface points will lead to changing the gap form. In consequence of this process, the dissolution rates will level off. As a result, a stationary gap form is to be achieved, at which the dissolution rate values are the same at all the reaction surface points. The rate of crystal material dissolution is determined by the stationary agent flux to the sample surface. To determine the dissolution rate (that is the rate of material chemical cutting), we developed a physical model for process of material removal at string CC [2]. The model is based on the assumption that equilibrium can be established between the chemical, diffusion and convection flows of the active etchant component at its motion from the tool to the surface of the sample being cut. For the stationary cutting mode the following dependence of cutting rate \( V \) on the principal technological parameters was obtained:

\[
\frac{1}{V} = \frac{\rho}{c_0 \beta} \left( \frac{l}{u \delta} + \frac{\delta}{D} + \frac{1}{\alpha} \right)
\]  

(1)

Here \( l \) is the cut length; \( u \) is the velocity of “cutting” tool motion; \( \delta \) is the minimal half-width of the gap between the sample and tool; \( c_0 \) is the chemical reaction rate constant; \( c_0 \) and \( D \) are, respectively, the concentration and diffusion coefficient of the active etchant component molecules; \( \rho \) is the density of the material being cut; \( \beta \) is the ratio between the mass of material dissolved during cutting process and that of the active etchant component required for its dissolving.

The parameters in expression (1) can be easily measured or estimated with rather high accuracy. The exception is parameters \( \alpha \) and \( \delta \) whose direct measurement is difficult to make. However, one can easily see that \( V \) as a function of \( \delta \) has a peak at \( \delta = \delta_0 \) where

\[
\delta_0 = \left( \frac{Dl}{u} \right)^{1/2} \tag{2}
\]

One can easily estimate \( \delta_0 \) value. Let the sample length \( l \) be 1 cm, the velocity of tool motion \( u \) be 20 cm/s (this is just the typical value for the conventional equipment) and the diffusion coefficient \( D \) be \( 10^{-5} \) cm²/s. Then, according to expression (2), \( \delta_0 = 7 \) µm. This value is rather small as compared to the tool section diameter (usually 100-200 µm). Therefore, if the tool carries rather big amount of etchant, then the cutting rate will be close to the maximal removal rate. The latter can be found by inserting expression (2) for \( \delta_0 \) into expression (1):

\[
\frac{1}{V} = \frac{\rho}{c_0 \beta} \left( \frac{l}{u \delta} + \frac{1}{D} + \frac{1}{\alpha} \right)
\]

(3)

As to the \( \alpha \) value, for reactions that obey diffusion kinetics (this is the optimal case for CC) it is very high, so one can ignore the second term in expression (3).

Let us estimate the limits for increasing operation efficiency of the CC technique that can be achieved in practice. From expression (3) it follows that, at rather high values of the chemical reaction rate, the removal rate is given by the following expression:

\[
V = k_1 u^{1/2}
\]

(4)

where

\[
k_1 = \frac{c_0 \beta}{2 \rho} \left( \frac{D}{l} \right)^{1/2}
\]

(5)

while the inverse removal rate is

\[
\frac{1}{V} = k_2 l^{1/2}
\]

(6)

where

\[
k_2 = \frac{2 \rho}{c_0 \beta} (uD)^{-1/2}
\]

(7)

Thus, if the \( k_1 \) and \( k_2 \) values are known, it is possible to predict for the CC technique growth of operation efficiency with tool motion velocity, and to determine time required for ingot cutting when its size is increased.

3. Experimental procedure

We performed experimental studies of the CC operational efficiency when cutting InSb, CdTe and HgCdTe single-crystal samples. In all cases we used etchant of the following composition: 20% bromine solution in hydrobromic acid. During experiment several parallel grooves of the same depth were made one after another, and time required for this was measured.

The experiments on determination of the cutting rate as a function of the sample length (see expressions (6) and (7)) were performed using a CXP-2 machine for CC [3]. The cutting tool was a tungsten string (90 mm in diameter); the velocity of its motion was 22 cm/s.

The CXP-2 machine turned out to be of limited suitability for experimental check of expressions (4) and (5) (cutting rate dependence on the tool motion velocity). The reason was that the range of string motion velocity was too narrow. To make this range wider, we made an experimental plant that made it possible to bring the tool motion velocity up to 6 m/s (i.e., to increase it by a factor about 30, as compared to the highest value provided by

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the CXP-2 machine). The tool to carry etchant was a Lavsan (Soviet equivalent of Dacron) thread that was being rewound from one spool to another during the experiment. The tool motion velocity was found from the time required for the thread to be completely rewound (the same time determined the experiment duration). The amount of material removed was determined from the depth of the groove made during the experiment. The duration of each experiment was several seconds. During that time we had to make such a groove whose depth could be big enough to obtain results of reproducible results. That is why we used very short \( t = 500 \mu \text{m} \) cuts. Use of the samples whose lengths were extremely small was of interest also for determination of conditions when diffusion kinetics of CC process changes for chemical one.

To theoretically calculate the removal rate at CC, one has to know the numerical \( \beta \) values for the etchants and materials used. We determined these values experimentally for dissolution of InSb, HgCdTe and CdTe in 20% bromine solution in hydrobromic acid. A sample of material to be dissolved (whose weight was previously measured) was put into a reservoir that contained a known amount of etchant. After this the reservoir was sealed, and the sample in it was exposed to dissolution for several hours. Then the sample was taken out of the reservoir, dried out and weighed. After this the sample was put into the reservoir (with the remains of the etchant) anew, and the total procedure was repeated once more. The experiment continued until the result of weighing was the same as at the previous stage. This evidenced that process of dissolution has stopped. After this the \( \beta \) value was calculated from the following expression:

\[
\beta = \frac{m_1^s - m_n^s}{m_{Br}^s}.
\]

Here \( m_{Br}^s \) is the initial mass of bromine in solution; \( m_1^s \) and \( m_n^s \) are the results of the first and last weighing, respectively. The coefficients \( b \) that were determined in this way for InSb, HgCdTe and CdTe were 0.57, 0.72 and 0.52, respectively.

4. Experimental result and discussion

The experimental and theoretical curves giving the inverse cutting rate \( 1/V \) as a function of \( l^{1/2} \) are presented in Fig. 1. One can see from this figure that functional agreement exists between the theoretical and experimental curves: in the coordinates used they are straight lines. This fact confirms the validity of assumptions (on which our model is based) on character of the physico-chemical processes proceeding at CC. Some difference in line slopes may be due to the fact that our theoretical considerations served for estimation only, because we did not know the exact values of diffusion coefficient for bromine molecules in the etching solution used. Besides, bromine concentration in grooves seems to be below the set bromine concentration in the reservoir from which the etchant is coming to the tool. The reason is that some portion of bromine evaporates from the tool while coming to the sample.

Special attention should be given to the fact that the dependencies obtained at CC of different materials are close to each other. This is true for both (experimental as well as theoretical) dependencies. The reason for this may be that numerical values of the non-dimensional parameter \( \rho / \rho_{0} \) are practically the same for different materials: 16, 17 and 18 for InSb, HgCdTe and CdTe, respectively.

Shown in Fig. 2 are the experimental and theoretical dependencies of the cutting rate \( V \) on the square root of the string motion velocity \( u \): \( V = f(u^{1/2}) \). One can see that these dependencies remain linear up to the maximal velocity of tool motion (\( u = 6 \text{ m/s} \), i.e., even at this \( u \) value the process still is not restricted by chemical kinetics. This fact evidences that diffusion kinetics of the CC process can be retained; in other words, the dependence \( V = f(u^{1/2}) \) will remain valid at higher \( u \) values.
According to the experimental results obtained, the cutting rate magnitude approaches the value \( V \sim 3 \text{ mm/min} \). In this case the CC rate becomes comparable to the rates that are typical for the most popular and efficient abrasion cutting technique, namely, cutting by a diamond disc saw with inner cutting edge. The numerical discrepancy between the \( V = f(u^{1/2}) \) dependencies obtained theoretically and found from experiment lies approximately in the same range and is of the same sign as that for the \( 1/V \) on \( U^{1/2} \) dependencies. So one can assume that both the above discrepancies are of the same origin.

A correlation made between the theory and experiment has confirmed, by and large, the validity of theory and possibility to use it for prediction of CC technique operation efficiency when changing the process parameters. The dependencies obtained by us revealed big potential resources for increase of CC rate. To illustrate, at \( u = 20 \text{ cm/s} \) an InSb, HgCdTe or CdTe ingot (10 mm in diameter) can be cut with a CXP-2 machine for about one hour. Our calculations show that, if the thread motion velocity is increased up to 20 m/s, then cutting operation takes about as little as 1.5 h, even if diameter of the ingot being cut is \( \sim 60 \text{ mm} \). Thus the appropriate modification of equipment (involving, mainly, increasing velocity of the etching liquid carrier motion) could make the CC technique able to meet competition with the abrasion techniques in the technological lines for single crystals processing.

5. Conclusions

1. On the basis of the balance model for convection-diffusion processes that are proceeding at string CC we obtained an analytical expression for dependence of the CC limiting rate on process parameters at maximal etching agent use. A comparison between the obtained experimental and theoretical dependencies of CC rates for InSb, HgCdTe and CdTe samples on the string motion velocity and diameter of the sample being cut demonstrated good agreement of experimental results with model concepts.

2. The experimental dependence \( V = f(u^{1/2}) \) remains linear over the whole range measured, up to the maximal (6 m/s) velocity of tool motion. This fact evidences that diffusion kinetics of the CC process is retained even at very high values of tool motion velocity.

3. The maximal CC rate obtained in our experiments was approaching the value \( V \sim 3 \text{ mm/min} \), i.e., it was comparable to the rates that are typical for the most distributed and efficient cutting technique, namely, that using a diamond disc saw with inner cutting edge.

4. The results obtained reveal big potential resources for CC rate increase. Technical modification of the equipment (related primarily to increasing velocity of motion of the etching liquid carrier) will make the CC technique able to meet competition with the abrasion techniques in technological lines for manufacturing of semiconductor devices.

References