Paper

Quantitative Analysis and Influence of CO_2 Absorbed in TMAH Solution for Silicon Etching

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This paper presents the quantitative analysis and influence of CO_2 dissolved in TMAH for silicon etching. The etching rate on the (100) plane increases at first and then decreases with the increase of CO_2 concentration. The etching rate on the (110) plane decreases monotonously with the increase of CO_2 concentration. Although the etching rate on the (110) plane is higher than that on the (100) plane at ordinary conditions, this relationship is reversed at a certain quantity of CO_2 dissolution. The etch-stop appears at higher concentration of CO_2 dissolution. It was confirmed that changes of the silicon etching characteristics are caused by concentration of carbonate anions. The CO_2 dissolution has influence on the (100) plane and no influence on the (110) plane.

Key words: MEMS, TMAH, Anisotropic Etching, Carbon Dioxide

1. Introduction

Anisotropic silicon wet etching is a key technology for fabrication of 3-D Micro Electro Mechanical Systems (MEMS). The commonly used etchants are TMAH (tetramethyl ammonium hydroxide), EDP (ethylenediamine, pyrocatechol, and water) and KOH. In recent years, the most widely used etchant is TMAH due to good compatibility with the integrated circuit process and good selectivity to the passivation layers.

For TMAH, an issue of silicon etching stability for temperature and other environmental conditions remains now. As the size of MEMS devices is reduced rapidly, the improvement of the stability of TMAH on silicon etching rates has attracted a lot of attentions. It is known that some trace additions (e.g. oxidizers, metal anions, surfactants) can be used to improve and control the TMAH etching characteristics of silicon [(1)-(3)]. For the better stability of TMAH, we quantitatively investigated influences of CO_2 on orientation dependence of silicon etching, because CO_2 is one of the significant substances which changes etching characteristics of TMAH.

In this paper, the experimental conditions and CO_2 measurements are introduced in chapter 2. The experimental results are given in chapter 3. Chapter 4 provides some discussions on the changes of silicon etching rates. Conclusions of this paper are given in chapter 5.

2. Experiments

The purpose of the experiments are to clarify the influences of CO_2 on TMAH anisotropic etching of silicon. This experiments were achieved by two steps. The first step is to bubble the TMAH solution with CO_2 for various bubbling times (various content of CO_2) and to measure the concentrations of dissolved CO_2 in the TMAH quantitatively. The second step is to etch the specimens using the TMAH with various concentrations of CO_2 and to measure the etched depths, lateral underetching and surface morphologies.

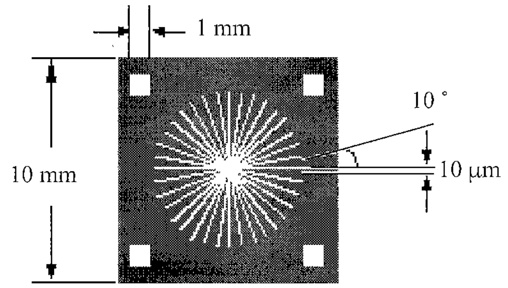

Fig. 1. Wagon wheel pattern

2.1 Etchant and Silicon Samples

The TMAH we used is produced by Toyo Gosei Kogyo Co., Ltd. in Japan. The concentration and pH value are 25 wt.% and 13.6, respectively. In the experiments, p-type silicon wafers with (100) and (110) surface orientations and resistivity of 0.1-100 Ωcm were used. Firstly the wafers were covered by a thermal oxide with thickness of 0.3 µm, and then the oxide layer was patterned for an etching mask. In order to obtain detailed data on the orientation dependences of etching rates, a wagon wheel pattern shown in Fig.1 was employed. The pattern consists of radial segments that are rectangular with the size of 10 µm x 8 mm. The segments are arranged in a fan shape with an angle of 10 deg. The size of the specimen is 10 mm x 10 mm square.

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2.2 Bubbling Process

The reaction between TMAH and CO_2 is an exothermic neutralization and the speed of this reaction is very fast[4]. The dissolution of CO_2 was achieved by bubbling the TMAH solution with CO_2 using a fine pipe (inner diameter of 1mm). The amounts of CO_2 dissolution were controlled by bubbling times. For obtaining the quantitative influence of CO_2 dissolution on silicon etching characteristics, 8 kinds of solutions with different CO_2 concentrations were used in every experimental step. In the experiments, after pouring 30 ml fresh TMAH solution into eight 80 ml test tubes, the CO_2 was introduced to the the TMAH solution at the bottom of test tubes. As the rising of CO_2 bubbles in the solution, the CO_2 reacts with and dissolves to TMAH solution. The flow rate of CO_2 was maintained at 1 ml/s. As the dissolution speed can be accelerated by heat of this neutralization, the test tubes were maintained at room temperature using a water bath.

At the beginning of the bubbling process, the size of CO_2 bubbles became smaller rapidly with the rising and the bubbles can not reach the top of the surface of TMAH solution. After several minutes, the bubbles appear at upper part of TMAH and its size becomes larger. Then some CO_2 is released from TMAH solution. This phenomenon indicates that the speed of reaction and dissolution begins to decelerate. After the CO_2 bubbling, CO_2 flow is stopped and switched to N_2 flow to blow the remained CO_2 away from test tubes.

2.3 Examination of CO_2 Concentrations

When CO_2 dissolves in TMAH, part of CO_2 is ionized to carbonate anions and bicarbonate anions. The remainder is only mixed into TMAH without ionization. The former contributes to the neutralization of TMAH and latter does not contribute it. The amounts of CO_2 dissolution were measured by two different methods: a weight method and a chemical precipitation method.

The weight method measures the difference of weights of TMAH solution before and after CO_2 bubbling. Thus the total amount of CO_2 can be measured regardless of ionization of CO_2.

On the other hand, the chemical precipitation method can estimate the amount of ionized CO_2, which contributes to neutralization of TMAH. When the ions of CO_2 (CO_3^{2-} and HCO_3^- anions) combine with some sufficient cations which can form insoluble precipitates, the anions are consumed by the formation of insoluble precipitates. Then the amount of ionized CO_2 can be calculated from the weight of the precipitation. In our experiments, $BaCl_2$ solution with concentration of 1 mol/ml was employed to react with CO_2 dissolved in the TMAH solution. When $BaCl_2$ solution is added into the TMAH solution, the Ba^{2+} cations combine to CO_3^{2-} anions to produce insoluble precipitates of $BaCO_3$. The amount of ionized CO_2 can be estimated from the weight of the precipitates extracted by filtration and drying process from the solution. Then the weights of dried precipitates of $BaCO_3$ were measured with a high precision balance and the weights of ionized CO_2 were calculated form the ratio of molecular weight.

Fig. 2 shows the obtained relationship between CO_2 concentration and bubling time from both the weight method and chemical precipitation method. The difference of the results between the two methods indicates the amount of non-ionized CO_2 in TMAH. In the following experiments, we will use CO_2 concentration from the chemical precipitation method.

There is a more simple estimation method for CO_2 concentration of TMAH[5]. It is a simple pH value measurement.

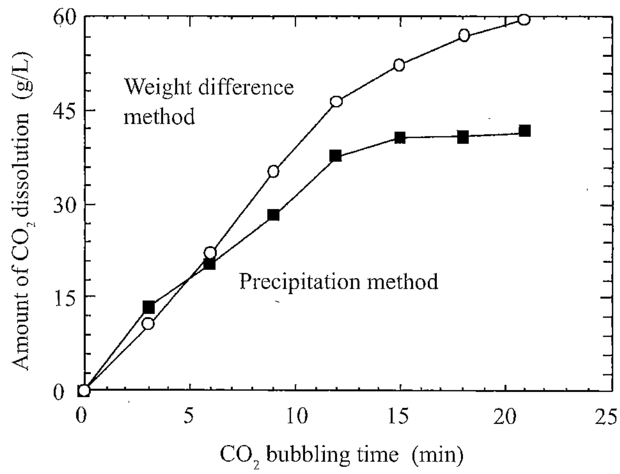


Fig. 2. Contents of CO_2 versus bubbling time.

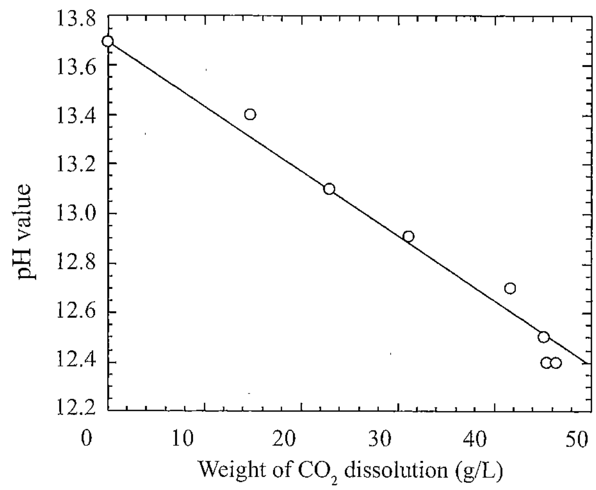


Fig. 3. pH value of TMAH solution.

This method depends on the neutralization and the pH value of alkali solution is reduced by the neutralizations. Fig. 3 shows the relation between the pH value and the concentration of CO_2 in TMAH. It shows an almost straight line. By measuring the pH value of TMAH, the concentration of CO_2 can be obtained from Fig. 3. Although the measurement accuracy is not high and it is not used in our analysis, it can be used for in-situ estimation of CO_2 concentration.

3. Experimental Results

3.1 Activation Energy of CO_2 Dissolution

The neutralization of CO_2 dissolution is a usual chemical reaction and its speed is a function of temperature. Fig. 4 shows the relation between reaction temperature and weight of dissolved (ionized) CO_2 in unit time and volume of TMAH. The weight of CO_2 dissolution was obtained by using the chemical precipitate method. In this measurement, the bubbling time is 3 min. and the flow rate is 1ml/s. The temperature of TMAH was varied from -5 to 10 deg C. From Fig. 4, we calculate that the activation energy of neutralization is about 0.14 eV. It is a large value for the gaseous reactants.

3.2 Influence of CO_2 Dissolution on Etching Rates

The silicon samples with the patterned SiO_2 film were immersed in the bubbled TMAH solutions to achieve anisotropic

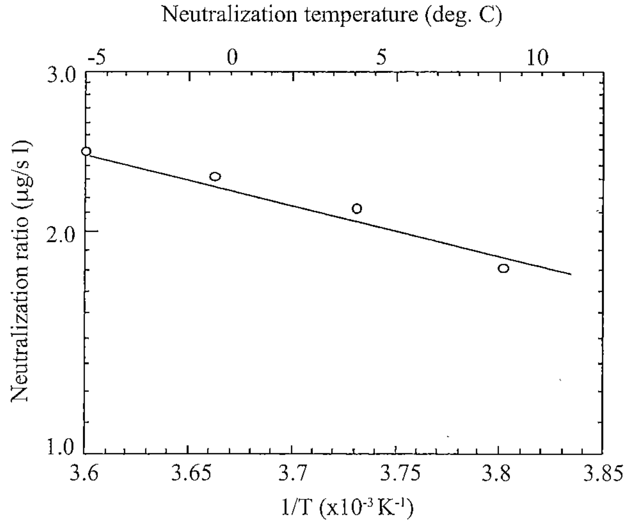


Fig. 4 . Activation energy.

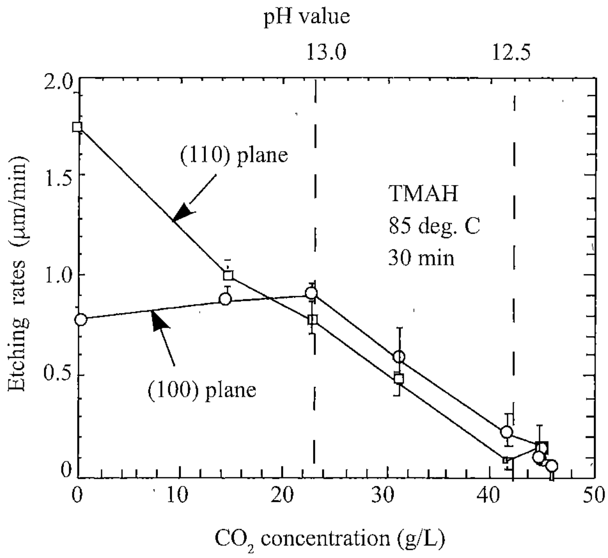


Fig. 5. The etching rates in various contents of CO_2 dissolution.

etching. The anisotropic etching was carried out at 85 deg C. for 30 minutes. After etching, the etched depths of the samples were measured using a measuring microscope. The etching rates of the (100) plane and the (110) plane were repeatedly obtained from three identical experiments. The mean values of etching rate are shown in Fig.5 with maximum and minimum values as the error bars.

As shown in Fig. 5, on the (100) plane the etching rate is 0.8 mm/min when CO_2 concentration is 0. This result confirms that the etching conditions in our experiments coincide with that cited in other papers[6]. Until the CO_2 concentration is 23 g/L, the etching rate of the (100) plane increases and reaches the maximum value of 0.9 mm/min. When the CO_2 concentration exceeds 23 g/L, the etching rate begins to decrease with the increase of CO_2 concentration. The CO_2 concentration of complete etch-stop is about 42 g/L.

On the (110) plane, the etching rate decreases monotonously with the increase of CO_2 concentration. Initially the etching rate is 1.7 mm/min that is the maximum value for the (110) plane. When the CO_2 concentration exceeds 40 g/L, the sample is not etched anymore and TMAH completely etch stops.

When the CO_2 concentration is about 18 g/L , the etching rates of the (100) plane and (110) plane are equal and their values are near 0.9 mm/min. When CO_2 dissolution exceeds this concentration, the etching rate on the (100) plane is higher than that on the (110) plane until to the etch-stop.

On the (100) plane, the lateral underetching values on the radial segments (on the all directions) were measured using the measuring microscope. The results are also shown in Fig. 6. The lateral underetching values on the (100) plane without CO_2 dissolution and with 23 g/L of CO_2 dissolution are shown. The lateral underetching rate of the <014> direction quickly decreases and the lateral underetching rate of the <001> direction decreases slowly with the increase of CO_2.

In Fig. 7, the lateral underetching values of the (110) plane are shown. The lateral underetching rates degrade quickly with the increase of CO_2 dissolution, at approximately equal ratio in all the

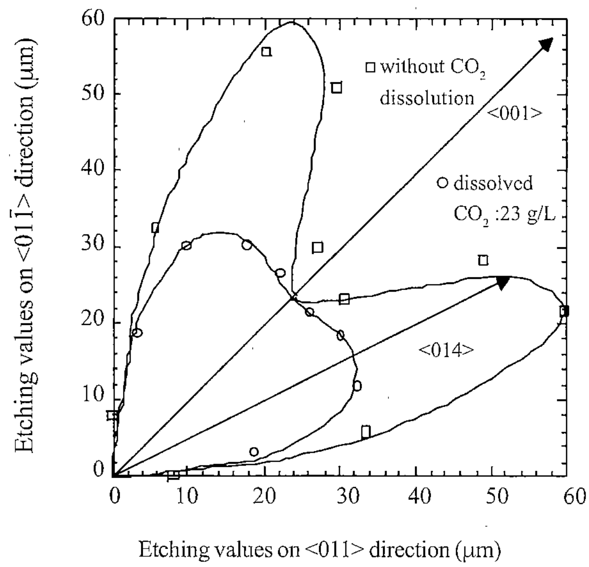


Fig. 6. Lateral etching values on (100) plane.

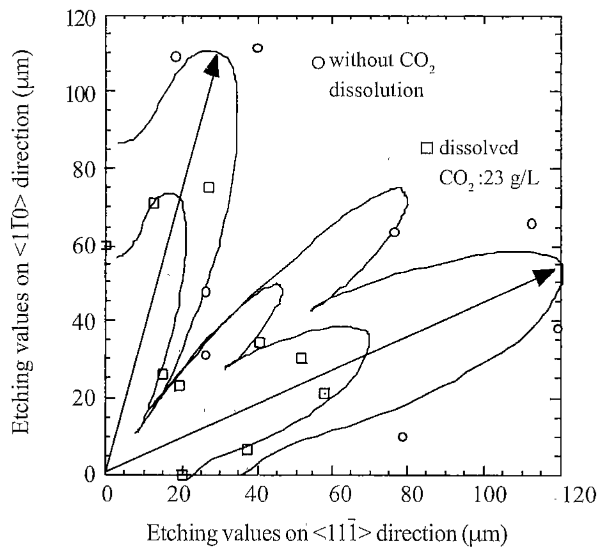


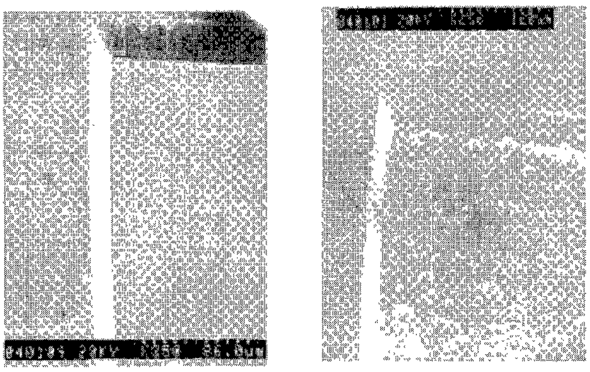
Fig. 7. Lateral etching values on (110) plane.

direction on the (110) plane.

3.3 Roughness of Etched Surface

The etched surface was observed by SEM and is shown in figure below. Fig. 8 shows the etched surface of the (100) plane in low CO_2 dissolution. The (111) side plane and the corner are clearly observed in Fig. 8. At the same time, the hillocks appear on the (100) plane. With the increase of CO_2 concentration, the number of hillocks increases. This phenomenon indicates that the products and the byproducts (e.g. hydrogen) have some influences on the surface.

When CO_2 concentration is high, the influence on (100) surface is different depending on the position as shown in Fig. 9. The etched bottom plane is covered by the hillocks completely. In the corner part of the pattern, unetched silicon is remained. This phenomenon is caused by gaseous products or the unreacted CO_2. The gaseous products or non-ionized CO_2 may create a temporary mask at the corner of pattern.



15 g/L 32 g/L

Fig. 8. Etched surface in low CO_2 concentration TMAH.

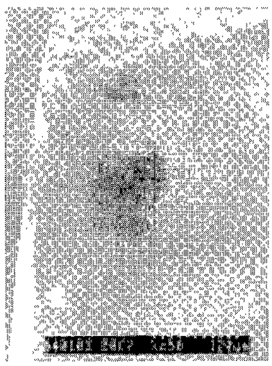


Fig. 9. Etched surface in high CO_2 concentration TMAH.

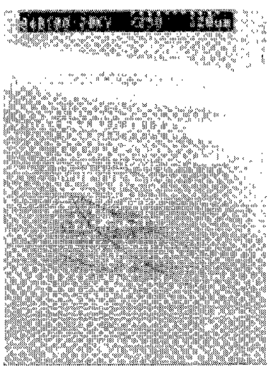


Fig. 10. The etched surface on (110) plane.

In contrast to the (100) plane, the etched surfaces of the (110) plane have no changes for eight different concentrations of CO_2 dissolution. All of the etched surfaces have a typical texture surface and show same roughness. No hillocks were formed on the surface of (110) plane while etching process (Fig. 10). It shows that the dissolution of CO_2 has no influence on the roughness of the (110) etched surface.

4. Discussions

The significant phenomenon in our experimental results is the change in the ratio of etching rates on (100) and (110) planes. Initially, the etching rate of the (100) plane is much higher than that of the (110) plane. As CO_2 dissolution increases, the etching rates of (100) and (110) become nearly equal and then both of them tend to zero.

The similar phenomenon of the change in etching rates can also be found in the case of K_2CO_3 or surfactant addition[2), (7)]. However, we used only CO_2 as addition and the etching mechanism is not directly similar to the case of K_2CO_3 or surfactant addition. In the following, we try to investigate this phenomenon further.

By dissolution of CO_2 in TMAH, following reaction is supposed to be dominant.

$$x[(CH_3)_4]OH + yH_2O + zCO_2 \Longrightarrow z[(CH_3)_4]_2CO_3 + (x-2z)[(CH_3)_4]OH + (y+z)H_2O \quad \cdots\cdots (1)$$

where non-ionized CO_2 is not represented in the equation. In the solution, $[(CH_3)_4N]_2CO_3$ and $[(CH_3)_4N]OH$ are ionized and generate CO_3^{2-} and OH^- ions. For accurate estimation, other products such as $[(CH_3)_4N]HCO_3$ and H_2CO_3 must be taken into account, however, we omit these products for simple discussions.

In our experiments, 25 wt.% TMAH is used. Thus x=2.75 mol/l and y=41.7 mol/l. The condition that $x=2z$ (all TMAH is decomposed and etching does not proceed any more) arises at z=1.38 which corresponds to the CO_2 dissolution of 60.5 g/L. In Fig. 5, the etching rates of (100) and (110) planes become zero when CO_2 concentration is around 45 g/L. Considering the electrolytic dissociation factor of TMAH, the etching stop at 45 g/L CO_2 concentration may be caused by lack of OH^- ions.

As the CO_2 concentration increases, the quantity of TMAH is reduced and H_2O slightly increases by the factor of $(y+z)$. Thus the concentration of the TMAH is reduced. Generally, the decreasing concentration of anisotropic etchant causes the increase of etching rate, because of the increase of H_2O which acts an important role to the etching mechanism together with OH^- ions. The solid lines in Fig. 11 are the rewrited form of the etching rates of (100) and (110) planes with respect to the TMAH concentration calculated from CO_2 concentration. In the figure, etching rates of TMAH without CO_2 dissolution, e.g. by diluting water, are also indicated by dashed lines[(6), (9)].

For the (100) plane, when TMAH concentration is higher than 15 wt.%, it seems that the change of etching rate of TMAH with CO_2 dissolution (solid line) completely follows the etching rate of TMAH without CO_2 dissolution (dashed line) and these is no influence of CO_2.

When the TMAH concentration became less than 15 wt.%, the

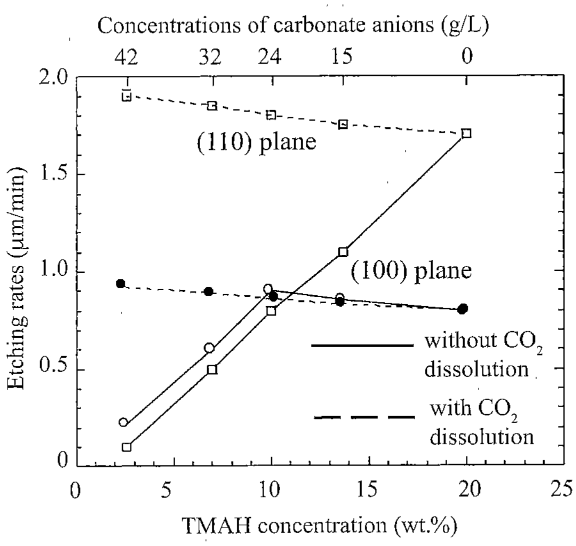


Fig. 11. The change of etch rate on (100) plane.

etching rate of TMAH with CO_2 suddenly decreases and separates from the etching rate of TMAH without CO_2. The critical value of CO_2, 24 g/L, corresponds to the point that the non-ionized CO_2 begins to mix to the solution (see difference between two curves in Fig. 2). So the non-ionized CO_2 may act as an etching mask for the (100) plane.

Contrary to the situation for the (100) plane, on the (110) plane the change of etching rate of TMAH with CO_2 dissolution is quite different from one without CO_2. Thus the reason of decrease of etching rate must be found from other compositions, such as CO_3^{2}. In the case of K_2CO_3 addition(7), also CO_3^{2-} ions appear in the solution. According to ref.(7), however, only 0.5 g/L K_2CO_3 addition causes large change in the etching rates. The quantity of 0.5 g/L K_2CO_3 corresponds to 0.0036 mol/l which is quite small contrast to our experiments (we dissolved CO_2 at an order of 10 g/L corresponding to 0.2 mol/l). Thus the influence of CO_3^{2-} ion is different from K^+ ions. We now assumes that the CO_3^{2-} ions effectively mask silicon (100) surface for the etching as same as the surfactant addition. The clarification of detailed mechanism is the problem to be solved in the next step.

5. Conclusions

The detailed effect of CO_2 in TMAH for silicon etching was examined. The etching rate on the (110) plane decreases with the increase of CO_2 dissolution. The etching rate on the (100) plane increases at first and then decreases with the increase of CO_2 dissolution. The both are equal for CO_2 concentration of 18 g/L. About the morphology of etched surface, the CO_2 dissolution has influence on the (100) plane and no influence on the (110) plane. It is confirmed the carbonate anions have strong influence on both of etching rates of (100) and (110) planes.

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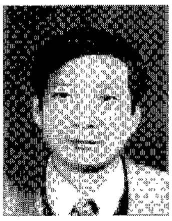

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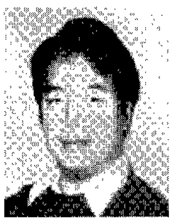

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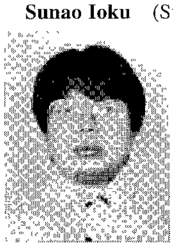

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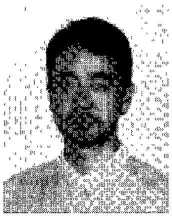

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