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Growth of diamond on silicon tips

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Abstract

The diamond films with (1 1 1) orientation were grown on silicon-tip arrays by microwave-plasma chemical vapor deposition (MW–PCVD). The diamond was preferentially grown on the top of the tips, and it can be explained as an effect of chemisorption on surface.

Keywords: Diamond; Field emission; Cold-cathode; Chemisorption

1. Introduction

Recently, diamond films on silicon-tip arrays have attracted a great deal of attention because they have good properties as field emitter materials [1]. For example, high thermal conductivity is favorable for high-currrent applications, and the electrons can easily escape from the surface of the diamond because of the property of negative electron affinity. However, it is important whether the diamond will be deposited uniformly on silicon tips. Hence, investigating the influence of the substrate morphology on the nucleation of diamond films is necessary. Denning and Stevenson [2] investigated the influence of substrate morphology on the nucleation of diamond, and found that the nucleation is favored on prominent features of the substrate [2]. Givargizov [3] obtained the same results and explained that the increase in nucleation on top of the tips was due to an increase of the temperature caused by localized recombination of hydrogen [3,4].

In this paper, we report the results of depositing diamond films on silicon tips, and consider that the increase of nucleation on apexes was caused by chemisorption on substrate.

2. Experimental procedure

The silicon-tip arrays were prepared on n-type (1 0 0)-oriented silicon wafers by oxidation,

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Fig. 1. Volcano tip arrays, inset is enlarged photograph.

photolithography and chemical-solution etching procedure. The volcano tips were formed by etching using nonpreferential etching mixture solution of $HNO_3 : HF : C_2H_5OH = 25 : 3 : 10$ for 20–30 min, and shown in Fig. 1.

The diamond was deposited on the silicon tips by MW–PCVD technique. The deposited conditions were as follows: The MW power was 450 W, the substrate temperature was about 850°C, the gas compositions were 1% methane in a balance of hydrogen, the vacuum pressure in the deposition chamber was 20 Torr during the deposition. The deposition process lasted for 2 h.

Before the deposition of diamond, some samples were abraded by diamond powder of 0.5 μm in diameter for 0, 5 and 10 min respectively, and then rinsed in deionized water with ultrasonic waves. The abrasion process, which will roughen the surface, is the usual method for increasing the nucleation of diamond. Using a small amount of diamond powder will reduce the destruction of the morphology of tips during the abrasion process.

The silicon-tip arrays and the deposited diamond films were observed by scanning electron microscopy (SEM). The orientation of diamond was measured by X-ray diffraction.

3. Results and discussion

Fig. 1 shows volcano-tip arrays, and the inset shows the enlarged photograph. The tips are about 3 μm high, and were not sharpened using thermal oxidize-etching process. The silicon wafer with tip arrays possesses several different regions, such as volcano crater, valley and flat region, and it is useful to investigate the influence of morphology on nucleation of the diamond.

Fig. 2 is a photograph of the diamond deposited on tips which were abraded for 5 min before deposition. It shows that quasi-continuous diamond films were formed on tip arrays. The diamond particles are about 1 μm in diameter, and the size is uniform. The black top is the tip's volcano crater. Same results were obtained from the samples abraded for 10 min before deposition.

Fig. 3 shows the diamond on the volcano tips. The diamond was grown on the nonabraded samples for 8 h under the same conditions. It shows that the diamond particles as large as 3 μm in diameter are usually grown around the tips, even coated a tip and few on the flat part, some on the conical side.

Fig. 2. Diamond on abraded tips.

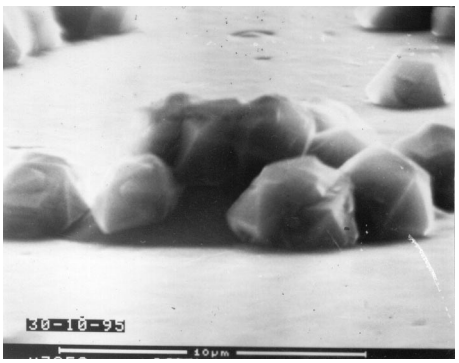

Fig. 3. Diamond deposited on no-abraded tips for 8 h.

Fig. 3 shows the nucleation of diamond has a preference for the top of the tips, but the preference was not found in Fig. 2, and the preference disappeared if the deposition time is short, which shows that the preference is weak. In the literature, some authors explained that the preference is due to an increase in temperature on apexes of tips that was caused by a recombination of hydrogen [4]. They used the hot-filament CVD technique to deposit the diamond film on the silicon tips and the temperature on the apexes of tips is higher than that of the flat region because the tips are about 70 μm high. But in our experiment, the tips were about 3 μm high, and the MW–PCVD technique made a uniform thermal field, the whole wafer including the top and the flat part was at the same temperature during the deposition of diamond. So the nonuniformity of thermal field can be neglected. The dominant factor influencing nucleation of diamond on the apexes is the chemisorption, not the increased temperature caused by recombination of hydrogen on top of the tips.

Usually nucleation of diamond can be increased on abraded rough surface. The silicon wafer with tip arrays is similar to a rough surface, but not as rough as the abraded surface. Therefore, the density of nucleation of diamond is smaller than that on a rough surface. But, in the two cases, the nucleation on both the top and the rough surface is due to the same mechanism.

For a material to be grown by CVD methods, the chemisorption on surface is the first step for crystal growth. The chemisorption would be enhanced on rough surfaces, because the rough surface provide more active sites in prominent features such as defects, broken bands, etc. that are able to adsorb the excited gaseous molecules [5]. Especially, the chemisorption plays a more important role in diamond CVD growth, because in the growth, the methane gas that has been used is decomposed to gaseous molecules such as C_2H_2, CH_3, etc. [6], which are adsorbed at the active sites on the silicon wafers and after a complex process the diamond will be formed. If the nucleation probability is related to the density of active sites, the density of active site is a constant for a nonabraded wafer with tip arrays and as the top-surface of volcano tip is cone-like, the following results can be obtained:

$$\frac{D_a}{D_f} = \frac{N_a}{N_f} = \frac{1}{\sin\theta}. \tag{1}$$

In the formula, 2θ is tip's vertex angle, D_a and D_f are the density of nucleation of diamond on the top and flat regions, respectively, N_a and N_f are the number of active sites on the tip of the top and flat regions, respectively. But the actual density of active sites such as broken bands will be raised on the top of the sharp tips because of little peripheral atoms, and is several times of that in the flat region, so Eq. (1) becomes

$$\frac{D_a}{D_f} = \frac{N_a}{N_f} = \frac{K}{\sin\theta}, \tag{2}$$

where K is a coefficient and $K \geqslant 1$. Therefore, there are more active sites (such as broken bands) on the tops and it facilitates the nucleation of diamond. The preference of nucleation of diamond on the tops shows that it is possible that the diamond films can be deposited uniformly on tip arrays through controlling the deposition condition.

X-ray diffraction of diamond film for the sample in Fig. 3 is given in Fig. 4. In Fig. 4, the silicon (1 0 0) peak was moved away. Only the diamond (1 1 1) peak on 44° appeared. It indicates that the diamond deposition was preferential to (1 1 1). But Fig. 3 shows that the diamond particles are not all (1 1 1) oriented, a few are (1 0 0) oriented. The (1 1 1) oriented diamond is preferable as an emitter, because the (1 1 1) oriented diamond has negative electron affinity [7].

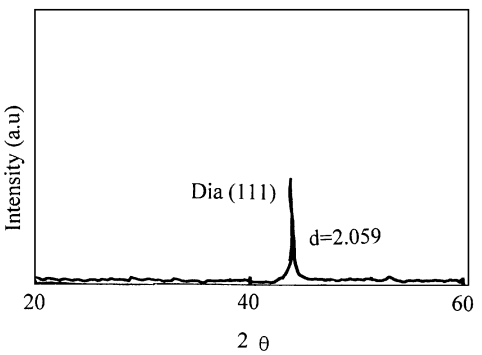

Fig. 4. X-ray diffraction of diamond films for the sample in Fig. 3.

4. Conclusions

Diamond-coated silicon-tips array as a material for field emission was fabricated. The diamond films with (1 1 1) orientation were preferentially deposited, and the apexes of tips have a superiority in nucleation of diamond, and it may be explained as a chemisorption effect on the surface. It is possible that the (1 1 1)-oriented diamond can be deposited uniformly on silicon-tip arrays as cathode materials.

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