

Development of nano-size mask for diamond emitter

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1. Introduction

The diamond is expected as an excellent material for electron emitter because it has negative electronic affinity.¹⁻³⁾ However, in conventional fabrication of diamond emitter using optical lithography the emitter size is several μm , therefore the emitter density can not be increased and the uniformity of the emitter height are not good. If nano-size masks can be formed on a diamond wafer, the uniformity of the emitter height will be increased and the emitter density can also be drastically increased. Moreover, since the emitter density determines the electron emission intensity, it is expected that the high intensity emitter can be fabricated. In this work we succeeded in forming two kinds of nano-size hard masks (TiN/Al and amorphous silicon) on a diamond wafer by electron beam (EB) lithography. As a result the high-density nano-size diamond emitter tips are fabricated.

2. Device Fabrication

Two kinds of dot-like hard masks onto 2-inch polycrystalline diamond wafers were fabricated as shown in Fig. 1. One hard mask is TiN/Al stack type and the other is made of amorphous silicon (a-Si). Firstly the Al (50 nm) and TiN (50 nm) films were deposited by the sputtering method or a-Si was deposited by the low-pressure CVD method onto diamond wafers. Next, the resist dot pattern was formed on the TiN/Al or a-Si layer by EB lithography, and then they were shrunk by the O_2 plasma ashing. The TiN/Al stack masks and a-Si masks were formed by reactive ion etching (RIE) using BCl_3+Cl_2 gases and CF_4 gas, respectively. Finally nano-size diamond emitter tips were formed

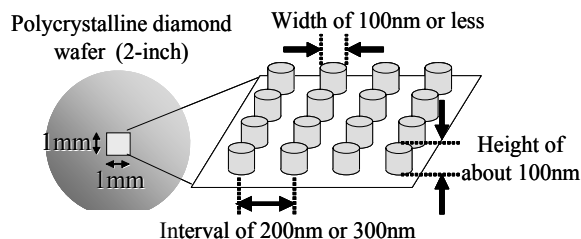


Fig. 1. Formation size of dots on diamond wafer

by etching diamond layer by means of reactive ion etching using O_2+CF_4 gases.

3. Results and Discussion

Figure 2 shows SEM images of top view of the TiN/Al stack mask dots fabricated on the diamond wafer ((a) and (b)) and side view of the mask dots fabricated on Si wafer (c) for its form check. The width of dots is about 100-110 nm, the height is about 80 nm, thickness of Al layer is 50 nm and TiN layer on it is 30 nm thick. In case that resist pattern is formed on TiN/Al layer by EB lithography, because of strong backscattering of electrons it is difficult to shrink the dot interval less than 200 nm.

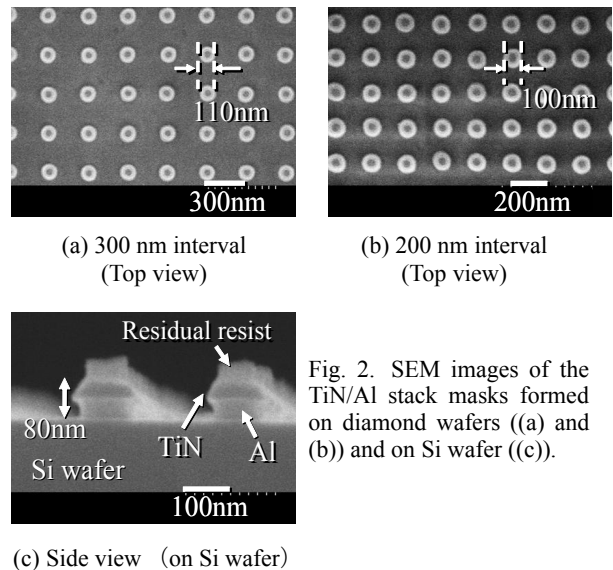


Fig. 2. SEM images of the TiN/Al stack masks formed on diamond wafers ((a) and (b)) and on Si wafer ((c)).

On the other hand, the shape of the hard mask is like a mushroom because the undercut of Al layer occurs by chlorine gas. Figure 3 shows the diamond tips fabricated by means of the TiN/Al stack masks. The shape of the formed diamond emitter is similar to a candle. This is due to the hard mask with form like a mushroom as shown in Fig. 4.

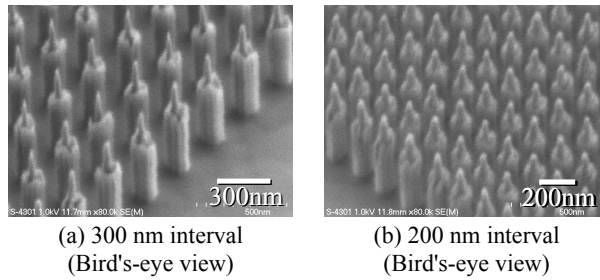


Fig. 3. SEM images of diamond emitters fabricated with the TiN/Al stack masks.

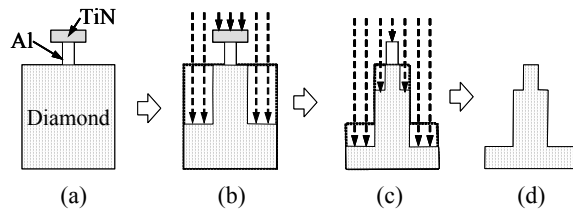


Fig. 4. Etching process of diamond layer by means of the TiN/Al stack type mask. Firstly diamond is etched by TiN layer ((b)) and next by Al layer ((c)).

Figure 5 shows SEM images of top view of a-Si mask dots fabricated on the diamond wafer and side view of the mask dots fabricated on Si wafer for form check. The width of a dot is 45-80 nm, and the height is about 75 nm. In contrast to fabrication of TiN/Al stack mask, the backscattering of electron in exposing by EB lithography is not so strong that it is easy to control the size of small resist pattern, and reproducibility is also good. So, still higher-density dots are also expected.

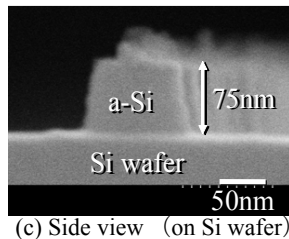
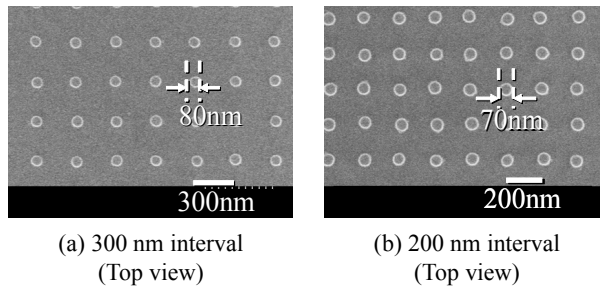


Fig. 5. SEM images of the a-Si masks formed on diamond wafers ((a) and (b)) and on Si wafer ((c)).

Figure 6 shows the diamond emitters fabricated by means of a-Si hard masks. The emitter width is smaller than the hard masks and its form is very

thin needle type. Width of emitter tip is 20 nm or less and the size of the root of the emitter is 30 nm.

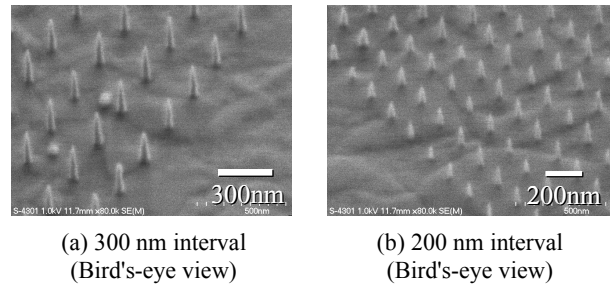


Fig. 6. SEM images of diamond emitters fabricated with the a-Si masks.

4. Conclusion

We succeeded in forming two kinds of nano size hard masks, TiN/Al stack type and a-Si one onto a polycrystalline diamond wafer using electron beam lithography. And then using these hard masks, two kinds of nano-size diamond emitters, candle type and needle type, were fabricated. The emitter density is 25 piece / μm^2 (200 nm interval) and the dispersion of height of emitter is 5 % or less.

Acknowledgement

Nano-size masks fabrication in this work was carried out at Research Center for Nanodevices and systems, Hiroshima University, supported by the "Nanotechnology Support Project" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT). The etching of diamond was carried out at Semiconductor R&D Lab., Sumitomo Electric Industries, supported by "the Advanced Diamond Device (ADD) Project, which was cosigned by New Energy and Industrial Technology Development Organization (NEDO).

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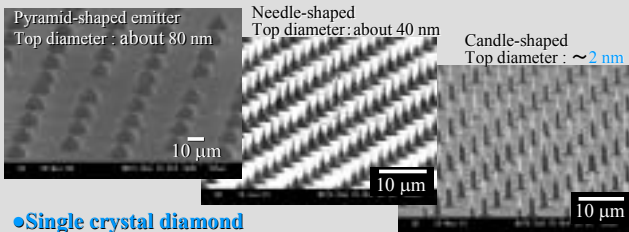
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Introduction

Diamond is expected as an excellent material for electron emitter because it has negative electronic affinity.

Sumitomo Electric Industries, LTD.

It is succeeded in forming various acute emitter with small tip diameter.



●Single crystal diamond

Issue

In conventional fabrication of diamond emitter using **optical lithography** the emitter size is several μm .

- **The emitter density can not be increased.**
 (The emitter density is less than 0.09 pieces/ μm^2)
- **The uniformity of the emitter height are not good.**
 (The dispersion of height of emitter is more than 25 %)

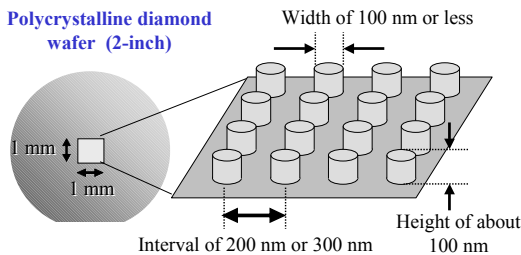
Solution

Fabrication of nano-size hard mask by means of electron beam (EB) lithography

Then, it is easy to form nano-size diamond emitter because processing technologies of diamond have already developed.

Hard masks fabricated in this work

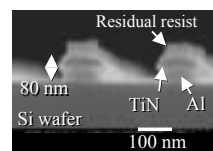
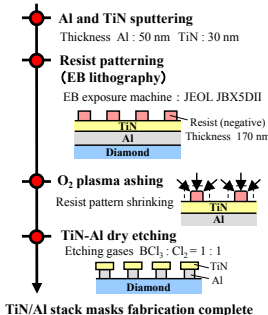
1. **TiN/Al stack type dots**
 A thing into which the aluminum mask was developed further.
2. **Amorphous Si (a-Si) dots**
 Amorphous silicon can be deposited easily at low temperature.
 Compared with Al, detailed processing of a-Si is easy.



Formation size of dots on diamond wafer

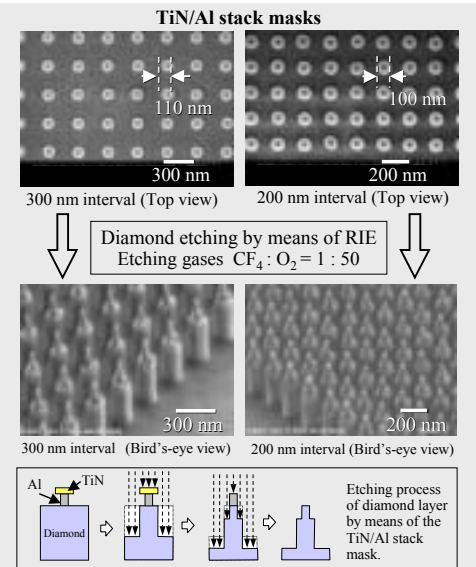
Fabrication of diamond emitter using TiN/Al stack masks

Fabrication process of the TiN/Al stack masks



Side view of the TiN/Al stack masks formed on Si wafer for form check.

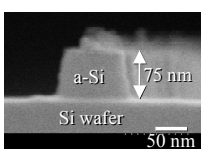
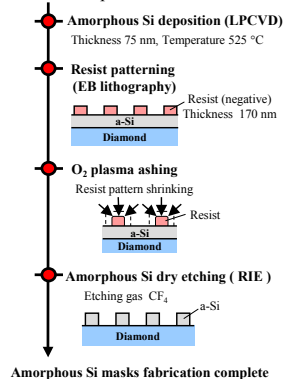
The shape of the hard mask is like a mushroom because the undercut of Al layer occurs by chlorine gas.



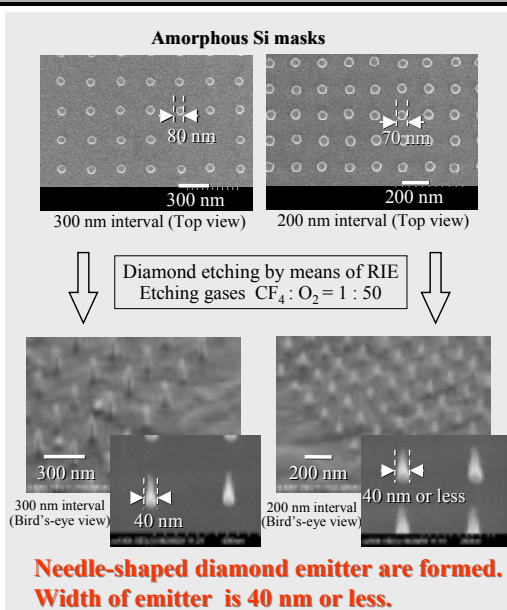
Candle-shaped diamond emitter are formed.

Fabrication of diamond emitter using a-Si masks

Fabrication process of a-Si masks



Side view of a-Si masks formed on Si wafer for form check.



Needle-shaped diamond emitter are formed. Width of emitter is 40 nm or less.

Conclusion

- We succeeded in forming two kinds of nano size hard masks, TiN/Al stack type and a-Si one onto a polycrystalline diamond wafer using electron beam lithography.
- Then using these hard masks, two kinds of nano-size diamond emitters, candle type and needle type, were fabricated.

•The emitter density:

Less than 0.09 pieces / μm^2 in convention

→ **25 pieces / μm^2 (200 nm interval) in this work**

•The dispersion of height of emitter :

More than 20 % in convention

→ **5 % or less in this work**

Acknowledgement

Nano-size masks fabrication in this work was supported by the "Nanotechnology Support Project" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT). The etching of diamond was supported by "the Advanced Diamond Device (ADD) Project, which was cosigned by New Energy and Industrial Technology Development Organization (NEDO).