論文内容の要旨

論文題目 Focused electron beam-induced processing: Size and composition

（集束電子ビーム誘起プロセスに関する研究：サイズと組成に関して）

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I. Introduction

In this thesis, investigations of focused electron beam-induced processing (FEBIP) were carried out with the objective of achieving a better control and understanding of this method. To that end, I carried out (1) more in-depth investigations of *in situ* stage current monitoring during the etching process for the size control of nanoholes and (2) enhanced the reactivity during deposition process by adding plasma chemistry to the conventional FEBIP. All the FEBIPs investigated in this thesis were carried out inside a conventional scanning electron microscope (SEM; S3600N Hitachi Co.) with a tungsten filament as electron source. The precursors were directed to the substrates by a microtube. Exposure time and position of the FEB in the SEM were controlled by lithography software (Xenos lithography software, Xenos semiconductor technologies GmbH).

II. Investigation of the size (Nanohole fabrication by etching)

In this part of my work, I realized a simple and one-step etching technique which allows the fabrication of nanoholes into 10-nm-thin amorphous carbon (a-C) membranes, which were chosen as a model material. Time resolved stage current was monitored during process as an end point detection. Monte Carlo (MC) simulations and knife edge measurements were performed to rationalize the experimental results. An a-C membrane was located on the Faraday cup in order to measure the stage current as precisely as possible.

The membrane surface became rough during the first irradiation seconds and the absolute stage current decreased. This is probably due to the increase in secondary electron emission from the surface accompanied by the roughening of the surface (edge effect). For increasing exposure times, both nanohole diameter and the absolute stage current increased. Finally, the hole diameter saturated, and the stage current saturated at almost the same value as the primary beam current (within a few %).

Considering the current balance of the system, the primary beam current I_P can be expressed as the sum of the currents of backscattered electrons I_{BSE}, secondary electrons, I_{SE}, and the measured stage current, I, yielding to:

$$I = I_P - I_{BSE} - I_{SE} \approx I_P - I_{SE} \qquad (1)$$

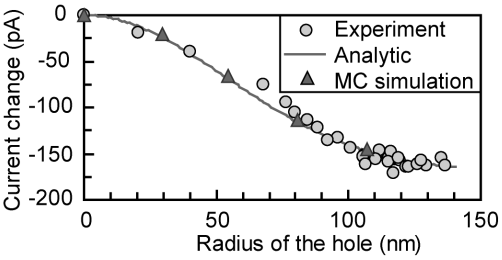

Fig. 1: *Variation of stage current as a function of hole radius. Analytic and MC models allow to determine the FWHM of the incident beam.*

Since almost all primary electrons penetrate into the 10-nm-thin membrane, I_{BSE} can be neglected and the balance is governed by the secondary electron emission. As a first approximation, assuming that primary and secondary electrons have the same radial Gaussian distribution, the secondary electron emission as a function of the radius R of the nanohole can be derived as:

$$I_{SE}(R) = \delta\left(2\pi\sigma^2\right) j_{peak} \exp\left(-R^2/2\sigma^2\right) \quad , \qquad (2)$$

where δ is the secondary electron yield, σ is the standard deviation, and j_{peak} is the peak current density of the primary electron current density distribution. The evolution of the measured current with the hole radius yields $I(R)$ - I(R = 0) = - {I_{SE}(R) - I_{SE}(R = 0)}. In Fig. 1, an experimentally obtained $I(R)$ - $I(R = 0)$ curve was fitted using eq. (2) by varying σ and δ values. Since the MC simulation agreed well with the analytical fit, the edge effects seem to be negligible. The secondary electron yield $\delta = 0.18$ obtained for the a-C membranes is comparable to reported values in the range of $\delta = 0.164$-0.501 obtained for a primary electron energy of 5 keV [1]. Thus the FWHM of the incident primary electron beam was estimated to be $2\sigma(2\ln2)^{1/2} = 125$ nm, in this case and it agreed well with the knife edge measurement. The smallest controllable ratio of minimum hole diameter to beam size was 0.2. The sub-beam size diameter of my nanoholes can be attributed to the low aspect ratio and the time-resolved *in situ* control of the etch process.

In the investigation of the size in FEBIP, nanoholes with diameters having only 20%-40% of the beam size were fabricated in a single step process using an in situ time resolved stage current control. The beam size of the primary electron beam was determined by precise and numerical interpretation of *in situ* stage current monitoring. This new probe size measurement technique might be useful not only for measurement of electron beams, but also for the assessment of focused ion beams which is normally difficult to be realized by the conventional beam size measurement such as knife edge measurement.

III. **Investigation of the composition** (Dot fabrication by deposition)

In this section, the increase of chemical reactivity during a conventional deposition was investigated through the deposition of copper dots with the assistance of a H_2/Ar plasma using copper(II)hexafluoroacertylacetonate (Cu(HFA)$_2$; $C_{10}H_2CuF_{12}O_4$) as a precursor. For the development of the process, (a) microplasma system operating under high vacuum conditions was developed at first, and then (b) conventional deposits were post-treated by the developed microplasma source to investigate the effect of the plasma and finally (c) microplasma was generated continuously during the deposition process.

A microplasma system working under high vacuum conditions (10^{-5}-10^{-1} Pa) and that can be operated inside an SEM, was at first developed. I employed a thermoelectron-enhanced microplama (TEMP), in which a tungsten filament is inserted into a miniaturized inductively coupled plasma source, allowing a stable plasma generation [2]. On the basis of fluid-dynamics simulations (CFD ACE+, ESI Group), the pressure in the area where the plasma was generated can reach up to 10^3 Pa by making the nozzle tip thinner, calculations having been conducted for a chamber pressure of 10^{-2} Pa. In the chamber pressure of 10^{-2} Pa, generated Ar TEMP was very stable, with less than 5% fluctuation of optical emission intensity at specific Ar lines over 3 hours. The atomic oxygen flux at the torch nozzle from O_2/Ar plasma measured by quartz crystal microbalance was revealed to be in the order of 10^{19} atoms/cm^2 s, which is 10^2 to 10^4 times higher than what has been obtained by other conventional plasma sources [3]. This localized and high-flux radicals/ions gun seemed to be suitable for rapid materials processing together with focused electron beam. Furthermore, the ability of low power generation suggests only minimal influence of the electromagnetic field on the FEB, which sometimes has to be controlled in sub-nanometer resolution.

The reduction of carbonaceous contamination has sometimes been investigated by (1) deposition in oxidative atmospheres such as water and oxygen, and (2) post annealing of the deposit in an oxidative atmosphere. Since only noble metals can be used in such investigations, oxidation free methods have been seeked, which would allow a wider choice of materials. Micron-sized FEIB Cu rectangles were at first deposited on Si substrates, then the samples were irradiated by the H_2/Ar plasma for a periods between 5 and 60 min. To take advantage of more ions from plasma, bias was applied on the substrates (-30 - +20 V). Fig. 2 shows the atomic content in the microstructure as a function of substrate bias during plasma irradiation. There seemed to be no influence on oxygen and fluorine contents after treatment. When a positive bias was applied, the atomic content of copper slightly increased from 11% to 15% and that of carbon decreased from 62% to 55% after 30 min of irradiation. The atomic content seemed to be unaffected from a positive substrate bias. On the other hand, the atomic content of carbon reduced to 36% and that of copper more than doubled (27%) with a decrease of the applied bias to -30 V. In the case of chemical sputtering [4], the threshold energy for Ar ions was reported to be several eV and the total sputtering yield increased with increasing substrate bias. This phenomenon seemed to be appropriate for my results.

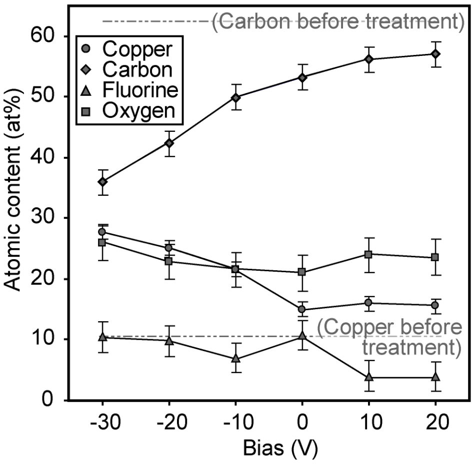

Fig. 2: *Atomic content as a function of applied substrate bias during post plasma treatment. (Plasma was irradiated for 30 min on conventionally fabricated rectangles.)*

Microplasma assisted (MPA) deposition was investigated to induce chemically active radicals and ions into conventional deposition method. To avoid interference of the electromagnetic field generated by the plasma source on the FEB, the plasma system was shielded. Figures 3 (a) and (b) show SEM images of fabricated deposits tilted by 60 degrees (a) without and (b) with H_2/Ar plasma treatment, respectively. The dot shape deposit with similar base diameter ($\approx 1.4\ \mu m$) was successfully fabricated by MPA deposition in FEB spot mode. However, the broad and thin deposit was also observed with a thickness of approximately 250 nm in the plasma irradiated area and has to be avoided in the optimization of the process. The growth rates were 13000 and 4000 nm^3/min, in the case of conventional deposition and MPA deposition, respectively. Furthermore, the atomic content of copper remarkably increased by the combination of FEB with plasma from 12% to 41% while other contaminating elements such as carbon, oxygen and fluorine decreased (Table 1). The decrease in deposition rates of MPAFEBID was probably due to lower contamination in the deposits.

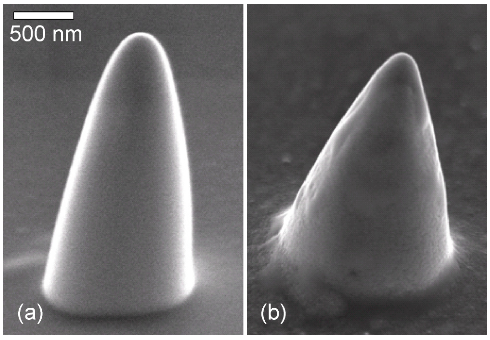

Fig. 3: *SEM images of deposits tilted by 60° fabricated (a) conventionally in 20 min and (b) MPA deposited structure in 90 min.*

The investigation of the composition in the deposit after and during the FEBID was carried out using a newly developed microplasma source. Both post and in situ (MPAFEBID) H_2/Ar microplasma treatment showed an increase of the copper content. Compared to previous approaches using oxidative media such as water and oxygen, these oxygen free approaches can be useful for the improvement of electronic properties of the deposits.

Table 1: **Results of EDX.**

Element	Conventional	**MPA**
Cu (at%)	12	**41**
C (at%)	59	**45**
O (at%)	23	**13**
F (at%)	6	**0**

IV. Conclusion

Focused electron beam induced processing for the better understanding and control with respect to size and composition was investigated in this thesis. In the investigation of size, sub-beam sized nanohole etching was achieved and in situ stage current monitoring during process correlated well with the nanohole growth not only as an end point detection. The numerical evaluation of the etch hole growth also allowed us to conduct beam size measurement not only for FEB but also for other focused charged particle beams. On the other hand, the metallic content of the FEBI deposits increased by post H_2/Ar plasma treatment of the conventional FEBI deposits and in situ MPA deposition in the investigation of composition. These oxidation-free improvements of the metallic content in deposits opened windows for a wider range of applications using FEBIP.

References

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