A New Method to Prepare Minimum-Mass Tin EUV Targets

GE Liqin, NAGAI Keiji, NORIMATSU Takayoshi, NISHIMURA Hiroaki, NISHIHARA Katsunobu, FUJIOKA Shinsuke, MIYANAGA Noriaki, MIMA Kuniok, IZAWA Yasukazu

Institute of Laser Engineering, Osaka University, 2-6 Yamada-oka, Suita, Osaka, Japan

E-mail: knagai@ile.osaka-u.ac.jp

Abstract. Minimum-mass target is an effective way to control debris produced during 13.5 nm EUV emission. In this work, we introduce a new method to fabricate 500 µm PVA air bubbles which is the supporting medium for tin layer using our home-made apparatus. We found that the thinner needle could produce smaller PVA bubbles at a stirring speed of > 420 rpm and the air bubbles were found to be stable more than 40 min which satisfies the requirement of EUV target. Tin elements were assembled on the PVA air bubbles and the presence of tin was confirmed by ICP experiment. The stability of the PVA air bubbles shows that they could be used as EUV emission target in the future.

1. Introduction

Extreme Ultraviolet Lithography (EUVL) is one of the key technologies to fabricate integrated circuits [1-4]. For the projection lithography, the 13.5 nm is chosen since the Mo/Si multilayer coated mirror used in this experiment shows very high reflection of about 70% around this wavelength. In this content, it is important to prepare efficient EUV target material for projection lithography. Various materials, such as Li, Xe and Tin were used to prepare EUV target materials with high conversion efficiency (CE) and power [3-5]. Laser-produced tin plasma is an attractive 13.5 nm light source due to its compactness and high emissivity with a highly intense emission peak at 13.5 nm. Thus much effort has been devoted to the development of the tin-based EUV light source. However, debris emitted from tin plasma damage and contaminate the first EUV collection mirror and degrade mirror reflectivity [6-8]. It has been shown the “minimum-mass target” to produce EUV light is an effective alternative method to eliminate the neutral atoms and low-ionized ions originating from the low-intensity wing of the laser spot as well as the deep layer from the target surface. This means that in a minimum-mass target almost all the atoms subjected to laser pulses could be converted into highly charged ions without additional emission of neutral atoms and other debris from the target [9-11].

In most case, tin bulk targets were irradiated with large spot size of the order 500 µm using the fourth harmonic of a Nd:YAG laser and investigated the EUV emission from tin plasma. The 500 µm laser spot was chosen to exclude energy losses due to the lateral expansion. The experiment with large spot size is also important to provide databases for comparison to theoretical predictions [12]. Minimum-mass targets consisting of tin layers of 10–1300 nm thicknesses deposited on a plastic hollow sphere (thickness ≈ 7 µm and diameter ≈ 500 µm) and was irradiated with a focused laser to produce EUV light [12]. The hollow plastic sphere is a supporter in the minimum-mass target.
In the present investigation, our aim is to establish a simple method to fabricate polyvinyl alcohol (PVA) air bubbles and then load tin layer on the bubbles and use as a EUV target. We have studied the influence of injection speed, stirring speed, needle pore size and surface modification to control the size of PVA air bubbles and their lifetime.

2. Materials and methods
2.1 Materials
Polyvinyl alcohol (PVA) was purchased from Sigma with a molecular weight 20,000. Poly(styrenesulfonate, sodium salt) (PSS, $M_w$ 70,000) and poly(allylamine hydrochloride) (PAH, $M_w$ 70,000) were from Aldrich. The water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus 185 purification system and the water show a resistivity of higher than 18.2 MΩ cm$^{-1}$.

2.2 Methods
The air bubbles were produced by injection of air into 7% PVA aqueous solution through the home-made apparatus as shown in Scheme 1. The volume of the syringe is 1 mL. The pump can tune the injection speed by the syringe and the needle pore size can control the size of the bubbles. Three kinds of needles with a diameter about 1 mm, 0.5 mm and 0.3 mm were used in this experiment. The image of the bubble was recorded with optical microscope.

2.3 Fabrication of tin contained air bubbles
After the bubbles were produced, they were dispersed into 1 mg/mL PAH and 1 mg/mL PSS solutions, alternatively. Excess polymer was removed by water wash. Then the PVA air bubbles were dispersed into 20 mg/L SnSO$_4$ solution and excess tin on the surface was removed by water.

2.4 Measurements of plasma spectrometer ICP
The bubbles were broken and the tin was measured by ICP (SPS 7800, Plasma-spectrometer, Seiko Instrument Company). In order to transfer the bubbles completely, the container was washed with 10: 90 H$_2$SO$_4$/H$_2$O (v/v).

3. Results and discussion
The PVA bubbles were prepared using the apparatus as shown in Scheme 1. The PVA air bubbles were produced with a stirring speed of 329 rpm using two kinds of needles with diameter 1 mm and 0.5 mm. Fig. 1 shows the microscopy image of the PVA air bubbles and they are symmetric and homogenous. The influence of needle size and injection speed on the bubble size was studied and the results are shown in Fig. 2. Fig. 2 clearly shows that the obtained bubble size is smaller than a thinner needle (0.5 mm) used. The injection speed was found to influence the size of the bubbles. When 1 mm needle was used, the bubble size was found to increase with the injection speed. When an injection speed of 1 mL/min and 0.5 mm
needle were maintained, the smallest bubble of 1.8 mm was obtained. The lifetimes of the 3 mm and 2 mm bubbles were studied and the results are shown in Fig. 3. The lifetimes of 30 bubbles were studied and it was found that they disappeared within 5 min after they were produced. Such short lifetime can not satisfy the requirement of EUV target, which is about 30 min.

Fig. 1. The optical microscopy image of the PVA air bubbles.

Fig. 2. The effect of the injection needle size and speed on the bubble formation.

Fig. 3. The lifetime of 2 mm air bubbles. The lifetime was followed by taking 30 bubbles.
It is understood from the observation that the air bubbles with < 500 µm size could not be produced with 1 mm and 0.5 mm size needles. So, the third type of needle was introduced with pore size about 0.3 mm. The 500 µm air bubbles with the lifetime higher than 45 min were obtained in this method. Such air bubbles satisfy the requirements of EUV target.

The bubbles were dispersed in 1mg/mL PAH and PSS solutions alternatively, and this procedure was repeated for three times. This pre-treatment of the air bubbles is expected to improve the stability and the adsorption of tin ions on the bubbles. The pre-treated air bubbles were dispersed in 20 mg/L SnO₂ solution and washed with water to remove the excess tin ions. The obtained bubble was broken for ICP analysis and washed with 10 : 90 H₂SO₄/H₂O (v/v) to collect the solution. The ICP result showed a concentration of 1.6 ppm of tin and this result confirmed that tin could be assembled on the bubbles successfully.

**Conclusions**

Minimum-mass target is an effective way to control the debris produced during 13.5 nm EUV emission. In this work, we have shown that the 500 µm PVA air bubbles could be formed and tin ions could be assembled on the bubbles using our home-made apparatus. We have shown that the thinner needle could produce smaller bubbles at a stirring speed of > 420 rpm. The obtained air bubbles showed longer than 40 min lifetime which satisfies the requirement of a EUV target. Three bilayer PAH/PSS were fabricated on the air bubbles which make tin to be assembled on the capsule easily. ICP result confirmed that tin was assembled on the bubble successfully. Further work is progress to use this tin contained bubbles as EUV target.

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