Nuclear Instruments and Methods in Physics Research B xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Micro-structuring of epoxy resists containing nanoparticles by proton beam writing

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ARTICLE INFO

Article history:
Received 31 August 2016
Received in revised form 9 December 2016
Accepted 23 January 2017
Available online xxxx

Keywords:
Proton beam writing
Epoxy
Resists
Nanocomposites
Nanoparticle

ABSTRACT

Proton beam writing (PBW) on SU-8 composites with nanoparticles (size: 14–750 nm) of silver, silica, alumina, and carbon with concentration of 5.0 wt% was studied aiming for high-aspect-ratio micro-structuring. Results of SRIM simulation suggest that deep micromachining of more than 100 μm is possible by 3.0 MeV PBW with increase in lateral straggling of less than 5.0%. Sensitivity loss of 150% was observed by introduction of 5.0 wt% nanoparticles to SU-8. There is a correlation between the sensitivity loss and volume concentration of nanoparticles. We fabricated pillar arrays of SU-8/silver nanocomposites with 10 μm in diameter and 80 μm in height by PBW at 3.0 MeV. Cross-sectional observation of the SU-8/silver pillar arrays shows that silver nanoparticles are homogeneously dispersed in SU-8, while aggregation was observed at the side surface.

1. Introduction

Proton beam writing (PBW) [1] has been applied to a wide variety of materials including not only resists [2–4], but non-resist materials such as semiconductors [5] and polymers and plastics [6–9], since the radiation effects by MeV protons can induce reactions of bond scission or cross linking reaction due to the high linear energy transfer.

One of the characteristics micro-structuring by the PBW is the deep penetration depth with straight trajectories of the protons inside the materials due to the large mismatch in the mass of protons to electrons in materials [1]. This feature enables deep, high-aspect-ratio micro-structuring applicable for unique applications such as microfluidics [10–13], optical waveguides [14–16], micro-lens arrays [8,17], etc. Even a drawback of PBW as a direct write serial process can be overcome by combined use of imprint lithography [18–20].

Nanomaterials in various forms such as particles, wires, tubes, etc. have attracted attention due to its superior and unique properties such as optical, magnetic properties [21]. If one can add the nanomaterials into materials such as plastics and rubbers while keeping the original natures [22], we can obtain functional nanocomposites [23,24] with the addition of nanomaterials with desired functions.

Motivated by the wide variety in the choice of functional nanomaterials and the unique features of PBW, we studied the effects of nanoparticles in the epoxy resists aiming at micro-structuring of nanocomposites. We take advantage of high-sensitive resists for PBW with functionalities of filler materials, while other lithographic techniques, EB and UV lithography are susceptible to scattering or absorption of the embedded fillers. Proton beam writing has a potential to micro-structuring of these composites by MeV-protons with straight trajectories in materials. The filler materials should be small enough (<1 μm) for micro-structuring.

The present study is aiming at the micro-structuring of SU-8/nanoparticle composites by PBW. A negative-tone, epoxy-based resist for PBW was used as a base polymer. Effects of additional nanoparticles such as silver, alumina, silica, and carbon were studied in terms of the sensitivity to MeV protons.

2. Experimental procedures

Nanoparticles such as silver, silica, alumina, and carbon with sizes ranging from 14 to 750 nm (see Table 1) were dispersed in anisole with a conventional ultrasonic bath for 20 min and then subjected to ultrasonic homogenizer (Hielscher, UP-50H) for

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http://dx.doi.org/10.1016/j.nimb.2017.01.068
0168-583X/

Table 1
Samples of SU-8/nanoparticle (silver, silica, alumina, and carbon) composites.

Sample name	SU-8	SU-8/silver	SU-8/silica	SU-8/alumina	SU-8/carbon
Diameters	–	<100 nm	10–20 nm	<750 nm	<100 nm
Density (g/cm^3)	–	10.5	2.2	4.0	2.0
Thickness (μm)	17.3	10.2	18.9	14.9	11.4
Vol% of particles	–	0.59	2.7	1.5	3.0

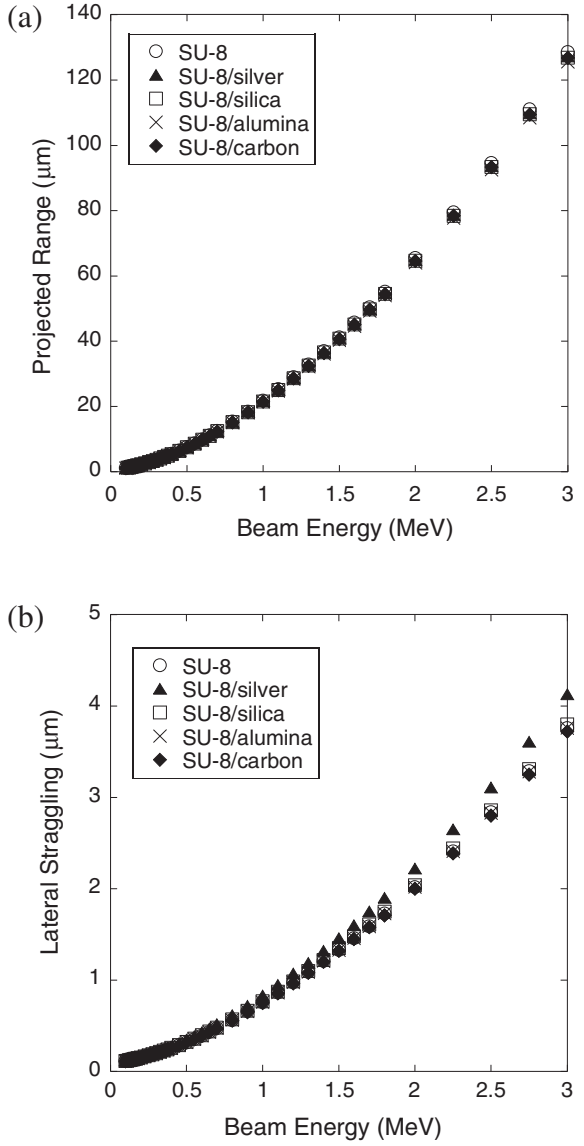

Fig. 1. SRIM simulation for SU-8 and SU-8/nanoparticles composites with 5.0 wt% in SU-8. Projected ranges (a) and lateral straggling (b) in SU-8/nanoparticles composites.

2 min. The nanoparticle suspension in anisole was mixed with SU-8 3025 (Microchem Corp.) as a base polymer using a planetary centrifugal mixer (THINKY Corp., AR-100) with concentration of 5.0 wt %. After these procedures, we observed a few droplets of the nanoparticles in SU-8 on a silicon wafer by an optical microscope. We found that the diameters of the visible particles in the SU-8 are less than 2 μm.

In order to avoid nanoparticle residues on the substrate after development, an SU-8 layer of ~1 μm was formed at 8000 rpm for 30 s on silicon substrate. Then, a SU-8/nanoparticle composite layer was spin-coated at 4000 rpm for 30 s. Prebaking steps were performed at 65 °C for 2 min and then at 95 °C for 10 min. As shown in Table 1, the resulting SU-8 thickness with different nanoparticles vary from 10 to 19 μm due to the viscosity change by the added nanoparticle suspension in anisole. For thicker SU-8/nanoparticle layer up to 100 μm, we performed repetitive spin-coating steps accompanied by subsequent prebake steps at 65 °C for 2 min and 95 °C for 2–8 min depending on the thickness.

Proton beam writing at beam energy of 1.0 and 3.0 MeV was performed using beamlines at Shibaura Institute of Technology and National Institutes for Quantum and Radiological Science and Technology, respectively. The beam spot size is focused to around 1.0 μm with beam current of 20–30 pA. After the proton beam writing, development process with a commercially available SU-8 developer (Microchem Corp.) was performed at room temperature for 10 min.

Microstructures formed by PBW were observed by a conventional SEM (Shimadzu, SSX-550). We observed nanoparticles at the side surface and the cross section in SU-8 by FE-SEM (JEOL, JSM-7400F) operated at 5 kV. We also extracted compositional and topographic information from the backscattered electrons. For observation of the nanoparticles inside the SU-8/nanoparticle, we obtained a cross sectioned using FIB (HITACHI, FB-2000A) operated at 30 kV equipped with a Ga liquid metal ion source.

3. Results and discussion

3.1. SRIM simulation

Fig. 1(a) and (b) show results of SRIM simulations [25] for SU-8 and SU-8/nanoparticles composites with 5.0 wt% in SU-8. From Fig. 1(a), the projected ranges of protons with energy up to 3.0 MeV into SU-8 is not significantly changed by introduction of 5.0 wt% nanoparticles of silver, silica, alumina, carbon.

On the other hand, the lateral straggling increases by around 5% for silver nanoparticles at 3.0 MeV. This is due to the contribution of silver with larger atomic number (Z = 47) than Si (Z = 14), Al (Z = 13), and C (Z = 6). These results indicate that deep, high-aspect-ratio micro-structuring up to a 100 μm depth is possible for SU-8 composites with 5.0-wt% nanoparticles.

3.2. Resist sensitivity

One of the important features of SU-8 as a negative-tone resist is high-sensitivity to proton beam [2]. We therefore studied effects of nanoparticles on the SU-8 sensitivity. By scanning 10-μm diameter circles with varied fluence from 1 to 100 nC/mm^2 as shown in Fig. 2(a), 10 × 10 pillar arrays of SU-8 and SU-8/silver composite were formed as shown in Fig. 2(b) and (c), respectively. We measured the height of each pillar to evaluate the sensitivity of SU-8 composites including those with other particles such as silica, alumina, and carbon.

We plotted in Fig. 3(a), the height of pillars as a function of fluence. We defined here sensitivity of the SU-8 composites as a fluence, at which the remaining thickness corresponds to 50% of total thickness. The sensitivity of SU-8 was lowered by the introduction of nanoparticles, as shown in Fig. 3(b).

Since these nanoparticles have no sensitivity to the proton beam, the effective sensitivity of the nanocomposite is determined by the volumetric density of SU-8, which is sensitive to the proton beam. Therefore, the sensitivity loss due to the introduction of nanoparticles is related with the volume concentration of nanoparticles, rather than the weight concentration. As shown in Table 1, the volume concentration varies for the same 5.0 wt% concentration of nanoparticles. If we define the sensitivity loss as the

Please cite this article in press as: R. Sano et al., Micro-structuring of epoxy resists containing nanoparticles by proton beam writing, Nucl. Instr. Meth. B (2017), http://dx.doi.org/10.1016/j.nimb.2017.01.068