Thin Solid Films 567 (2014) 54–57

Contents lists available at ScienceDirect

Thin Solid Films

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

Oxidative modification of imprinted nanopatterns assisted by heat and plasma

Dae Keun Park [a], Aeyeon Kang [a], Mira Jeong [b], JaeJong Lee [b], Wan Soo Yun [a,*]

[a] Department of Chemistry, Sungkyunkwan University (SKKU), Suwon 440-746, Republic of Korea
[b] Korea Institute of Machinery and Materials (KIMM), Daejeon 305-343, Republic of Korea

ARTICLE INFO

Article history:
Received 7 November 2013
Received in revised form 15 July 2014
Accepted 16 July 2014
Available online 25 July 2014

Keywords:
Nanoimprint
Nanopattern
Nanostructure
Oxidative etching
Chemical modification

ABSTRACT

We report on a simple and efficient linewidth modification of imprinted nanopatterns by heat and plasma assisted oxidation. Addition of oxygen was found to be critical in reducing the process temperature and the efficiency of the linewidth reduction. The linewidth defined by nanoimprint lithography (NIL) can be reduced more than 60% without any deterioration of structural details of the fine patterns. Weakened material dependence of this oxidative process was verified from the results obtained from the experiments adopting various materials. Furthermore, it was also demonstrated that this method could be applied in the modification of different types of nanopatterns prepared by the NIL.

1. Introduction

In recent years, demand for the fabrication of ultrafine nanostructures has increased in various fields including some frontier researches on nanophotonics and nanoelectronics [1–6], for instance. Among those methods proposed for the last 20 years, nanoimprint lithography (NIL) has attracted significant attention due to its great potentials in large-area fine pattern generation with a high throughput at relatively low cost [7,8]. Despite those potentials, however, the NIL is still suffering from some of its drawbacks including the high cost of the master mold and inflexibility of the pattern formation as well as the problems accompanied with the 'contact' nature of the fabrication process. Among them, the strongly-limited flexibility of the pattern shape is one of the most critical constraints on its application to the on-demand type pattern formation. Although there are some strategies reported addressing this issue [9–22], it is still quite demanding to devise the ways of achieving the pattern modification in a simple and reproducible way.

In this work, a simple and highly reliable method of modifying an imprinted nanopattern is reported. The linewidth of NIL pattern was efficiently and effectively reduced by heat and plasma treatment under oxygen environment. It was found that the combination of those heat and plasma treatments could yield a better result of nanopattern modification ensuring both the efficiency and the reproducibility and also that this method was applicable to a wide range of nanopatterns having different geometrical structures and chemical compositions. We hope that this method be regarded as an alternative strategy for the modification of ultra-fine nanostructures prepared by the NIL.

2. Experimental details

For line patterning, we have used an NIL mold made of polyurethane acrylate (PUA) whose nominal width and height were 70 nm and 140 nm, respectively. Using this mold, line patterns were imprinted onto three different polymers (SU-8 and Ormostamp from Microchem and Microresist Tech, PUA from Minuta Tech, and NIL system ANT-6H from KIMM) which were spin-coated on a silicon substrate and hardened conditions at 60 °C under the pressure of 189 MPa. The PUA stamp was removed after UV curing for 1 min. Dot and hole patterns were also prepared with the use of a PUA stamp under the same NIL conditions. Heat treatments were performed at 200–500 °C for 1–10 h and plasma treatments at 200 W for 10–80 s. In both of the treatments, the oxygen flow rate and the pressure were set to be 100 sccm and ~133 Pa, respectively. Structural characteristics of the resulting patterns were examined from the images obtained by a field emission scanning electron microscope (FEI Sirion 400) and transmission electron microscope (TEM, JEM-2100F) with 10 kV and 200 kV operating voltage, respectively. For cross-sectional TEM analysis, the sample was

* Corresponding author. Tel.: +82 31 299 4568; fax: +82 31 290 7075.
E-mail address: wsyun87@skku.edu (W.S. Yun).

http://dx.doi.org/10.1016/j.tsf.2014.07.023

prepared by focused ion beam system (Quanta 3D FEG) with cross-section milling of imprinted pattern at the Ga^{+} ion beam current of 40 pA.

3. Results and discussion

Fig. 1 shows the results of heat treatment with and without oxygen. The average linewidth of the initial SU-8 pattern was measured to be about 74 nm in Fig. 1a. When treated without oxygen at 300 °C, the linewidth reduction was quite limited, which is in good agreement with previous reports regarding the thermal decomposition behavior of polymeric structures [17,18]. In those reports, a temperature of around 300 °C seems to be a critical point under which the linewidth reduction of a nano-scaled polymeric structure by vacuum heat treatment is significantly restricted. As shown in Fig. 1b, heat treatment without oxygen for 5 h at a temperature of 300 °C reduced the linewidth of the SU-8 pattern by only 6–7%.

Further linewidth reduction was achievable by merely introducing oxygen to the heat treatment at otherwise identical conditions. In Fig. 1c, one can find that the linewidth reduction of the same SU-8 pattern was improved by a factor of four upon the introduction of oxygen (100 sccm, for this case). It should be noted that signs of deterioration of the pattern quality were not detected upon a further reduction of the linewidth by the oxygen-added heat treatment. Changes of the linewidth of the SU-8 patterns with respect to the duration of heat treatment, both with and without oxygen, are depicted in Fig. 1d. This figure clearly shows that the linewidth reduction rate was greatly enhanced with the introduction of oxygen. This improvement of the linewidth reduction rate was also observed at all temperatures above 200 °C (Fig. 1e). It, therefore, can be concluded that the introduction of oxygen gas is an effective way of accelerating the linewidth reduction process. At this point, one may expect that a much further reduction of the linewidth can be obtained by extended heat treatment time. It was revealed, however, that a further extension of the heat treatment (longer than 10 h) was not an effective way of obtaining a further reduction of the linewidth. Apart from concerns of possible damage from such a prolonged heat treatment, the rate of linewidth reduction became too small to be practical.

An efficient reduction of the linewidth can be achieved if the oxidative decomposition of the polymeric pattern is promoted by applying more reactive oxygen species. This was examined in the present work by adopting the oxygen plasma, and the results are displayed in Fig. 2. As shown in Fig. 2a and b, only a 30 s treatment of the oxygen plasma

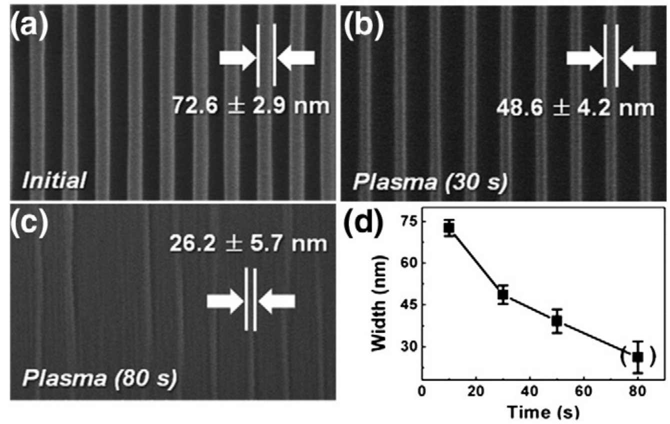

Fig. 2. SEM images of (a) an initial SU-8 pattern and the pattern after plasma treatment for 30 s (b) without and (c) with the oxygen flow. (d) Change of the linewidth with respect to plasma treatment time, which showed a strong enhancement of the reduction rate upon plasma treatment. The data point corresponding to 80 s is depicted in a parenthesis in order to indicate the irregularity of the plasma-etched line pattern at this condition.

reduced the linewidth of the imprinted nanopattern by about 33% (from 73 nm to 49 nm). When compared with the process of heat treatment, this is really an astonishing improvement of the efficiency of linewidth modification, which can be thought to be a result of the highly-energetic character of the plasma. Further reduction of the linewidth was easily attainable by simply extending the duration of plasma treatment (Fig. 2c, d). However, the structural stability of the polymeric nanopattern became lost upon extended plasma treatments. After 80 s, some portions of the line pattern were totally removed and, furthermore, the shape of the line became irregular and rough.

Comparing the results from the heat and plasma processes, it was possible to find a better strategy of linewidth reduction, which was efficient enough while not affecting the structural stability of the fine nanopattern: the combination of the two processes of heat and plasma treatments. A schematic of the combined process and the experimental results along with the process are shown in Fig. 3. The imprinted pattern was treated by plasma and heat consecutively under an oxygen atmosphere (Fig. 3a). As shown in Fig. 3b, c and d, the linewidth was decreased from 67 nm to 47 nm after plasma treatment for 30 s, and was further reduced to 28 nm by following heat treatment at 300 °C. It should be noted that the line pattern was not destroyed upon this combined treatment for the linewidth reduction. From AFM analysis,

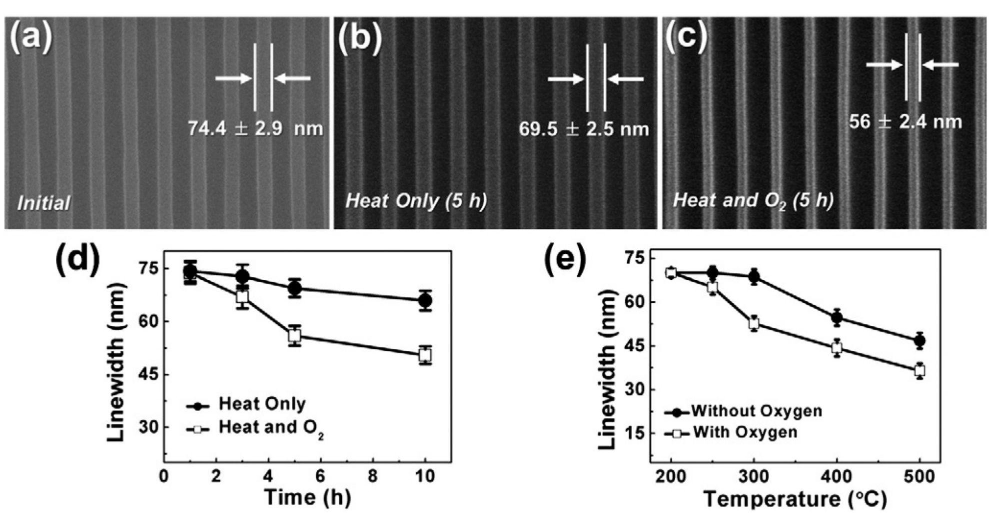

Fig. 1. SEM images of (a) an initial SU-8 pattern and the pattern after heat treatment at 300 °C for 5 h (b) without and (c) with oxygen flow. And changes of the linewidth along with (d) heat treatment time and (e) temperature showing an improvement of the reduction rate via the introduction of oxygen flow.