Microelectronic Engineering 123 (2014) 117–120

Contents lists available at ScienceDirect

Microelectronic Engineering

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

Defect analysis and lifetime evaluation of a release-coated nanoimprint mold

Masanori Okada, Daisuke Yamashita, Noriyuki Unno, Jun Taniguchi *

Department of Applied Electronics, Tokyo University of Science, 6-3-1 Niijuku, Katsushika-ku, Tokyo 125-8585, Japan

A R T I C L E I N F O

Article history:
Received 21 October 2013
Received in revised form 3 June 2014
Accepted 9 June 2014
Available online 26 June 2014

Keywords:
Nanoimprint lithography
Error rate
Contact angle
Release agent
Mold lifetime

A B S T R A C T

Nanoimprint lithography (NIL) is very useful technique for the fabrication of nanopatterns. In ultraviolet NIL, a release coating on the mold surface prevents the adhesion of the replicating resin. However, this release coating gradually deteriorates as the number of repetitions of NIL transfer increases. It is therefore important to evaluate the lifetime of the release agent. Measurements of the contact angle and release force are normally used in lifetime evaluation; however, these values do not clearly characterize the lifetime behavior because they tend to approach saturation as the number of repetitions increases. We introduce the error rate as a new means of evaluating the lifetime of release coatings. The error rate is derived by statistical treatment of transferred dots patterns. We found that mixing of various types of release agent is effective in reducing the error rate and, therefore, in increasing the lifetime of the NIL mold.

1. Introduction

Ultraviolet nanoimprint lithography (UV-NIL) is a very useful [1,2] technique for manufacturing nanoscale patterns such as antireflection films [3] and bit-patterned media [4]. However, during mass production, polymer adheres to the mold and errors occur in transferred patterns, even if the mold is coated with a release agent. Although adhering resin can be removed by a cleaning process, errors due to adhering resin are repeated, causing defects. To prevent adhesion of the resin to the mold, it is necessary to form a low-adhesion layer between the mold and the resin [5]. There are several techniques for forming release layers on molds for reducing adhesion [6–10]. In this study, we used a self-assembled monolayer formed by an organic thin film. However, the release coating on mold deteriorated as the number of repetitions of NIL transfer increased [11–17]. It is therefore important to evaluate the lifetime of the release agent. Lifetime is usually evaluated by measuring the release force and the contact angle [18,19]. However, these properties do not clearly characterize the deterioration behavior of the release agent, because they tend to reach saturation as the number of NIL transfers increases and, in this situation, it is difficult to identify a threshold value for the contact angle [20]. Therefore, to characterize the deterioration of a release-coated mold quantitatively, we introduced the error rate as a new assessment value. This error rate is acquired by statistical analysis of transferred replica dots patterns. The acceptable error rate is defined at being less than 0.0001%. This value is the same as the acceptable error rate for mass production of patterned media [21]. Here, we describe our evaluations of the lifetime of a release layer by measuring the contact angle and the error rate in a continually repeated imprint transfer.

2. Experimental apparatus and procedure

Silicon molds patterned with holes 230 nm in diameter and 230 nm deep (Scivax Co., Ltd., Kawasaki) were ultrasonically cleaned in acetone and ethanol successively for 15 min each; they were then subjected to cleaning with ozone for 1 h. The cleaned molds were treated with fluorinated silane coupling agents. In this study, we used OPTOOL DSX (Daikin Industries, Ltd., Osaka), trichloro (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) silane ($C_8H_4Cl_3F_{13}Si$; Sigma–Aldrich Japan Co., Tokyo), or mixtures of OPTOOL DSX and $C_8H_4Cl_3F_{13}Si$. The concentration of OPTOOL DSX and of $C_8H_4Cl_3F_{13}Si$ was 0.l wt%. In the case of the mixed OPTOOL DSX and $C_8H_4Cl_3F_{13}Si$, the concentration of OPTOOL DSX was 0.1 wt% or 1 wt% and that of $C_8H_4Cl_3F_{13}Si$ was 0.1%. The chemical structures of OPTOOL DSX and $C_8H_4Cl_3F_{13}Si$ are shown in Fig. 1(a) and (b), respectively.

The coating conditions were as follows: dipping time, 24 h; post-rinsing bake temperature, 120 °C; bake time, 5 min. The UV-curable resin that we used was PAK-01 (Toyo Gosei, Co., Ltd., Tokyo). The mold treated with the release agent was used in a repetitive UV-NIL process. Because the silicon mold is opaque to

* Corresponding author. Tel.: +81 3 5876 1440.
E-mail address: junt@te.noda.tus.ac.jp (J. Taniguchi).

http://dx.doi.org/10.1016/j.mee.2014.06.009
0167-9317/

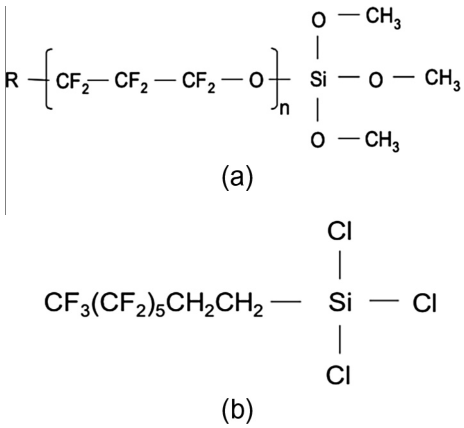

Fig. 1. Chemical structures of release agents OPTOOL DSX (a) and $C_8H_4Cl_3F_{13}Si$ (b).

UV radiation, the film was exposed to UV light through a polyester film to harden the UV-curable resin. The transfer force in the UV-NIL process was 20 N and the UV dose was 200 mJ/cm^2. The experimental process used in this study is illustrated in Fig. 2. The contact angle of the release-coated Si mold was measured at constant intervals by using contact angle-measurement equipment (Drop master-701, Kyowa Interface Science Co., Ltd., Niiza City). The transferred dots patterns were also examined at constant intervals by means of scanning electron microscopy (SEM). The error rate was calculated from the population proportion. In this study, we measured more than 100,000 replicated dots on the UV-curable resin, and this measurement gave a 95% confidence interval. The method used to measure the number of errors is shown in Fig. 3. To ensure that errors in the replicated pattern were easily identifiable, we choose a mold with a hole pattern. The measurement method was as follows. First, an SEM micrograph at a magnification of 4000× was obtained. Then, each error, such as that shown by the red circle in Fig. 3, was counted. The SEM field was then moved to another field at a given distance, a further SEM micrograph was taken, and the errors were counted as before. We measured 30 fields of replicated dots patterns and counted the total number of errors. These 30 fields of replicated dots pattern included more than 100,000 dots.

Statistical analysis of the error rate was performed by using the following expression:

$$\frac{m}{N} - 1.96\sqrt{\frac{\frac{m}{N}\left(1-\frac{m}{N}\right)}{N}} \leqslant p \leqslant \frac{m}{N} + 1.96\sqrt{\frac{\frac{m}{N}\left(1-\frac{m}{N}\right)}{N}},$$

where, m is the number of errors, N is number of samples (in this case, 114,570), and p is the error rate. The resulting error rate is expressed as a 95% confidence interval [22].

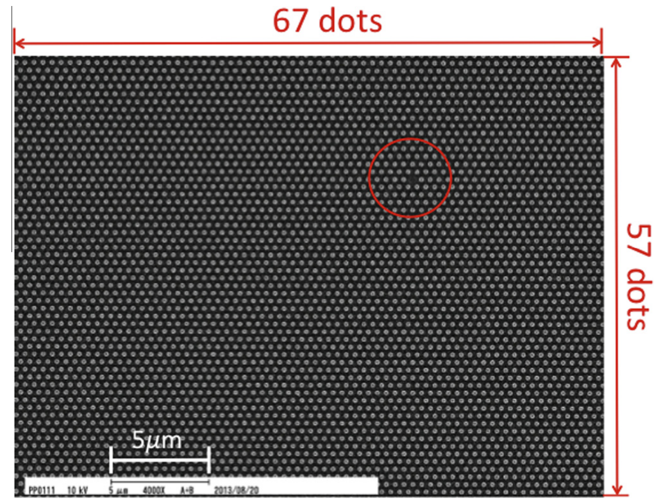

Fig. 3. The method for measuring the error rate. In this SEM image, 67 dots × 57 dots = 3819 dots. Different 30 fields of SEM images were observed. 3819 dots × 30 fields = 114,579 dots.

3. Results and discussion

The contact angle of the mold surface and the number of errors in the imprinted pattern were measured at constant intervals while a repetitive UV-NIL process was carried out. For each error measurement, more than 100,000 dots were examined by SEM, and the total number of errors in the pattern was determined. A typical transfer error is shown by the red circle in Fig. 3. We then calculated error ratio by statistical treatment as described above. Fig. 4 shows the relationship between number of repeated imprints, the contact angle, and the error rate for molds coated with OPTOOL DSX and with $C_8H_4Cl_3F_{13}Si$. The contact angles decreased as the number of repetitions of NIL increased for both release agents. The rate of deterioration of the OPTOOL DSX-coated molds was faster than that of the $C_8H_4Cl_3F_{13}Si$-coated molds. Furthermore, after about 400 repetitions of the NIL process, the OPTOOL DSX-treated surface showed adhesion to the UV-curable resin. Therefore, the lifetime of OPTOOL DSX is shorter than that of $C_8H_4Cl_3F_{13}Si$. However, the error rate for OPTOOL DSX-coated surfaces was less than that for $C_8H_4Cl_3F_{13}Si$-coated surfaces. OPTOOL DSX has a low friction coefficient and a low sliding force [23], which might contribute to the low error rate. If we consider the release motion of UV-NIL, as shown in Fig. 5, friction between the mold and cured resin occurs mainly on the side walls of the mold. Because OPTOOL DSX has a low frictional coefficient, we would expect this release agent to suppress the generation of errors. However, when OPTOOL DSX was used on its own, the coated mold had a short lifetime. To overcome this problem, we

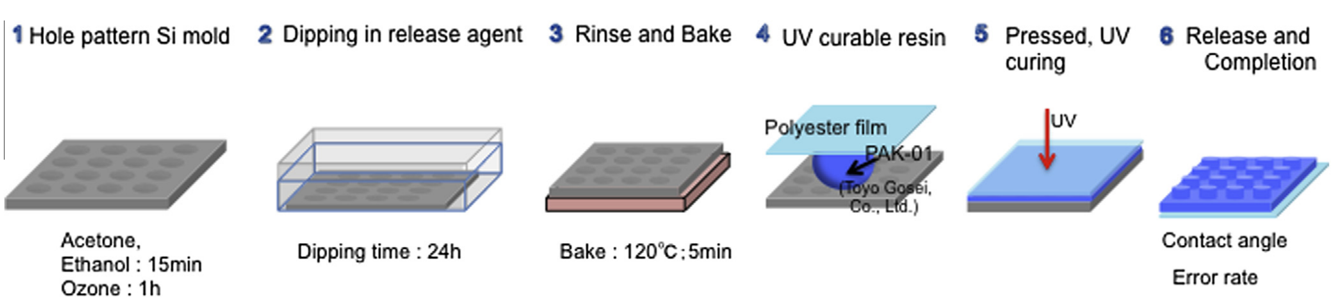

Fig. 2. Experiment process for release coating, UV-NIL, and mold evaluation.