Journal of Nonlinear Optical Physics & Materials
Vol. 19, No. 4 (2010) 773–779

DOI: 10.1142/S0218863510005698

IMPRINT-MOLD-CLEANING BY VACUUM ULTRAVIOLET LIGHT

MASASHI NAKAO

Nano ICT Group, Kobe Advanced ICT Research Center,
National Institute of Information and Communications Technology,
588-2 Iwaoka, Iwaka-cho, Nishi-ku, Kobe, 651-2492, Japan
Nakao_masashi@nict.go.jp

MASANORI YAMAGUCHI* and SHINTARO YABU

Project Promotion Department, Photon Process BU, Ushio Inc.,
1194 Sazuchi, Bessho-cho, Himeji, 671-0224, Japan
**m.yamaguchi@ushio.co.jp*

Received 12 October 2010

Imprinted molds which are contaminated by organic substances such as UV-resins through many times of imprinting processes are successfully cleaned with irradiation of a vacuum ultraviolet (VUV, $\lambda = 172\,\text{nm}$) light. Substrate temperature, radiation distance, and ambient oxygen concentration are also revealed as important factors to clean the molds.

Keywords: Vacuum ultraviolet; mold cleaning; imprint lithography.

1. Introduction

Imprint-lithography is expected to become one of the next-generation nanolithography techniques.[1–3] The imprint technology has been developing with the progress of the related components such as imprint-machines, -resins, and -molds. On the other hand, cleaning method of the imprint-molds is left unsolved. Repeatedly-used imprint-molds should be cleaned for the next series of imprint-lithography process using an appropriate cleaning method which results in defect-free patterning.

There are several methods for imprint-mold cleaning. Organic solvents and strong acids are frequently used under the ultrasonic condition. However, they are sometime difficult to remove residuals completely from the grooves of concavoconvex-patterned surface, and both methods have environmental problem in time of liquid waste disposal. Dry cleaning methods by ultraviolet (UV)-ozone and O_2-plasma are frequently used in the semiconductor process, because they are clean and easy. However, they are not effective in case of imprint-molds, which contain grooves and/or holes. Vacuum ultraviolet (VUV) is here adopted from the points of cleaning effectiveness and ecological technique.

Cleaning mechanism of VUV light is briefly introduced. It consists of two steps; the first is decomposition of organic materials ($C_xH_yO_z$) by VUV light with chemical bond dissociation energy of $h\nu$, and the second is oxidation by a singlet-oxygen, $O(^1D)$. Both reactions are shown by Eqs. (1) and (2), respectively.

$$C_xH_yO_z + h\nu \rightarrow C_{x'}H_{y'}O_{z'} \tag{1}$$

$$C_{x'}H_{y'}O_{z'} + O(^1D) \rightarrow CO, CO_2, H_2O \tag{2}$$

$C_{x'}H_{y'}O_{z'}$ represents chemical product of $C_xH_yO_z$ after breakage of chemical bonds, and the equations here are qualitatively shown. Then they are stoichiometrically incorrect. The singlet-oxygen is generated by following Equations of (3) and (4). Conventional UV light by mercury lamp also generates the singlet-oxygen by Eq. (3). On the other hand, VUV light generates the singlet-oxygen directly from oxygen by Eq. (4). Therefore, the cleaning by VUV is more than ten-times effective than that by UV.

$$O_2 + h\nu \rightarrow O_3, \quad O_3 + h\nu \rightarrow O(^1D) \tag{3}$$

$$O_2 + h\nu \rightarrow O(^1D) \tag{4}$$

Establishment of mold cleaning method is our final target.

2. Experimental Method

A cleaning machine equipped with Xe^* excimer type lamp, which is made by Ushio Inc.,[4] and which emits the light with wavelength of 172 nm, has been originally developed. The machine can control a VUV-exposure time (t_{VUV}), a substrate temperature (T_{sub}), an ambient oxygen concentration (c_o), and a radiation distance (d_{RD}). The cleaning procedure is as follows: (1) A sample is set on the plate at d_{RD}, and the sample room is closed. (2) The sample plate is heated up to T_{sub}, and c_o is controlled by nitrogen flow into the sample room. (3) VUV with power (P_{VUV}) is exposed on the sample for t_{VUV}. The samples are observed by optical microscope and SEM.

Four kinds of resins such as TR-21B for UV-imprint, PMMA for thermal-imprint, ZEP for electron-beam lithography, and AZ1500 for photolithography are used to measure the ashing characteristics. Two kinds of imprint-molds such as SiC for thermal-imprint and quartz for UV-imprint are used to examine the cleaning behaviors.

3. Results

3.1. *Ashing behavior of various resins by VUV-exposure*

In order to investigate the effectiveness of the developed VUV-exposure machine, various resins have been examined. Figure 1 shows dependence of the VUV-exposure time on the amount of thickness loss (= ashing amount) for various resins. VUV-exposure condition is $T_{sub} = 25°C$, $c_o = 20.9\%$, and $P_{VUV} = 10\,mW/cm^2$. Ashing

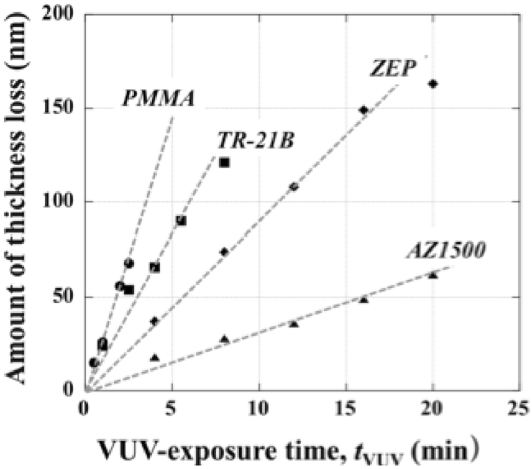


Fig. 1. Thickness loss of various resins by VUV-exposure.

rates are 3.2, 9.2, 17.0, and 29.4 nm/min for AZ1500, ZEP, TR-21B, and PMMA, respectively. The order of the rate is same as the well-known case of UV-ozone ashing. Imprint-related resins, i.e., PMMA and TB-21B possess relatively high ashing rate, which is positive meaning from the point of mold-cleaning. The ashing rates difference of about one-order magnitude between PMMA and AZ1500 may be useful in case of pattern transferring from AZ1500 to PMMA by VUV-light.

Figure 2 shows temperature dependence of thickness loss of ZEP resin under irradiation of VUV light. VUV-exposure condition is $c_o = 20.9\%$, and $P_{VUV} = 10\,mW/cm^2$. The results for three kinds of VUV-exposure time, i.e., 4, 12, and 20 minutes are presented in the Fig. 2. The higher substrate temperature is, the more effective ashing process becomes. VUV-ashing at 100° is ca. 3-times effective, as compared at room temperature.

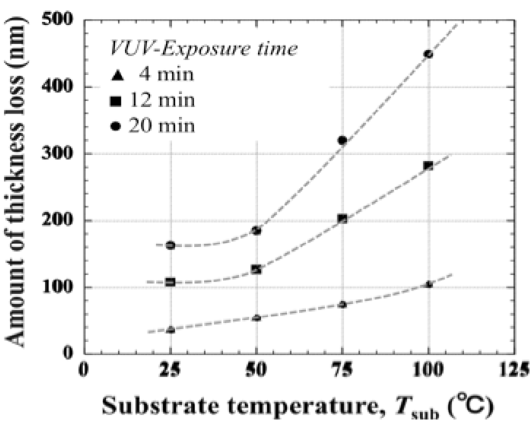


Fig. 2. Effect of Substrate temperature by VUV exposure.

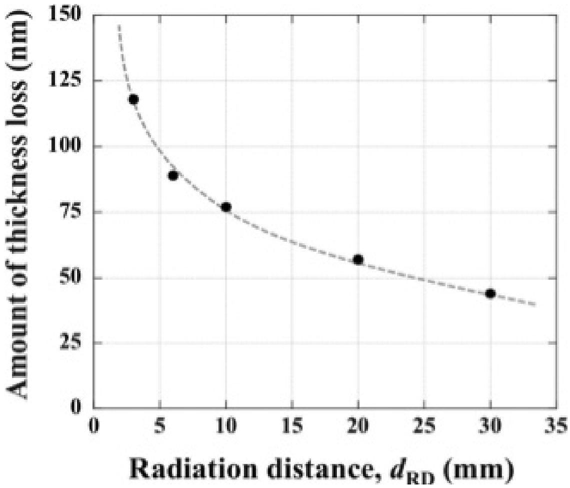


Fig. 3. Effect of radiation distance by VUV-exposure.

Figure 3 shows the dependence of VUV-exposure distance on the amount of thickness loss for ZEP. VUV-exposure condition is $t_{\mathrm{VUV}} = 4\,\mathrm{min}$, $c_{\mathrm{o}} = 20.9\%$, and $P_{\mathrm{VUV}} = 10\,\mathrm{mW/cm^2}$. The less d_{RD} is, the more VUV reaches to the sample surface, and the more amount of thickness loss becomes, because the singlet-oxygen generated in the vicinity of sample surface decomposes resins efficiently. The amount of attainable VUV to the sample surface is influenced by the ambient oxygen concentration. Next, the effect of oxygen concentration was examined for PMMA and ZEP as shown in Fig. 4. VUV-exposure condition is $T_{\mathrm{sub}} = 50°$, $t_{\mathrm{VUV}} = 3\,\mathrm{min}$, $d_{\mathrm{RD}} = 3\,\mathrm{mm}$, and $P_{\mathrm{VUV}} = 10\,\mathrm{mW/cm^2}$. Peaks of thickness loss of resin appear

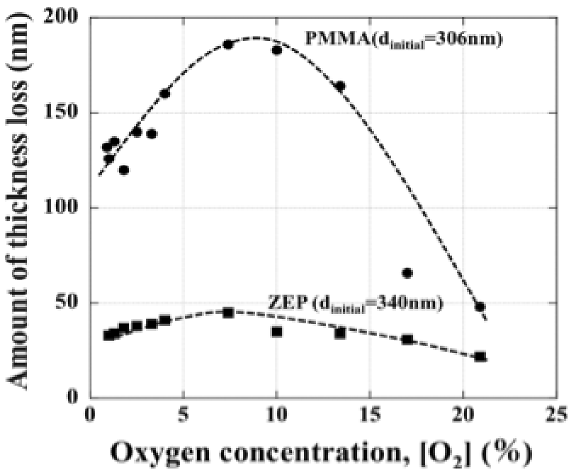


Fig. 4. Effect of ambient oxygen concentration by VUV-exposure.

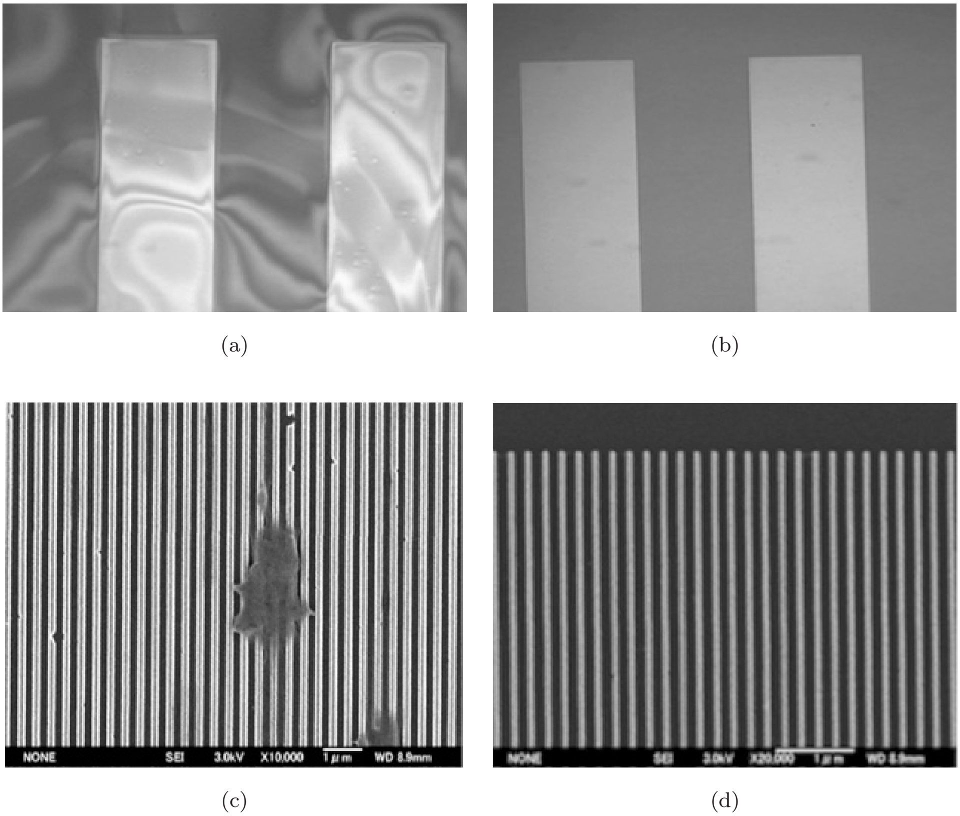


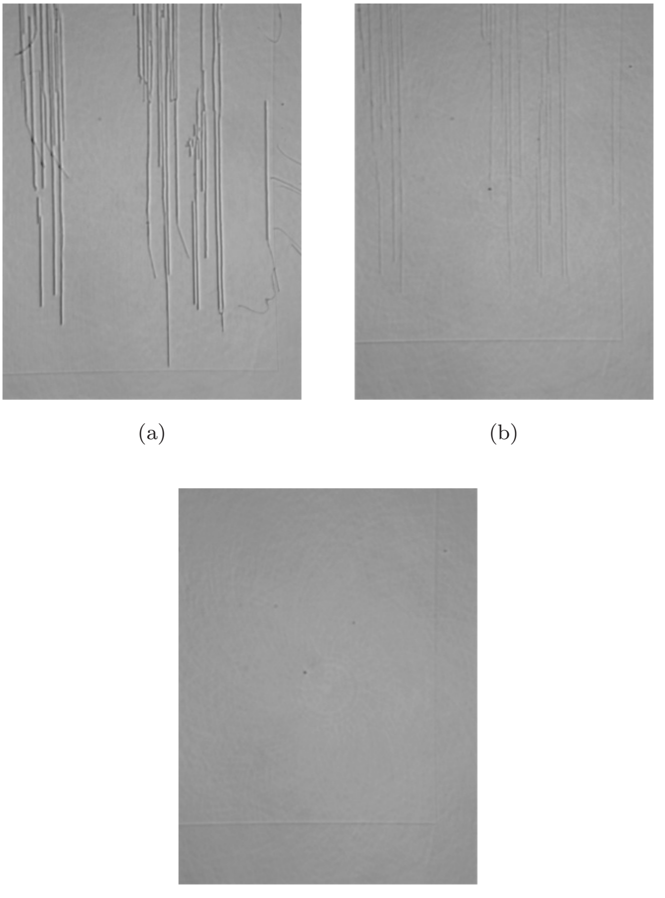
Fig. 5. Cleaning results of SiC mold.

at around 8% of oxygen concentration for both data of PMMA and ZEP. The reason for these peaks is understood under consideration of generation amount of singlet-oxygen in the sample vicinity. That is, under some distance condition (3 mm in the case of Fig. 5) the singlet-oxygen generating sample surface increases with increase of oxygen concentration. After reaching maximum point, further increase of oxygen concentration brings decrease of singlet-oxygen concentration because of strong absorption of VUV by oxygen before reaching to sample surface. As a result, ashing rate becomes maximum at around 8% of oxygen concentration. The different peaking-tendency of PMMA and ZEP is interesting. It indicates different interaction between VUV and individual resins.

The results obtained are benefit for mold-cleaning.

3.2. *Imprint-molds cleaning*

Successive cleaning results of imprint-molds by VUV exposure are shown in Figs. 5 and 6. The molds examined here are strongly contaminated by the imprint-resins. Figures 5(a) and 5(b) show pictures of optical microscope before and after 5-minutes



(a) (b) (c)

Fig. 6. Cleaning results of quartz mold.

VUV exposure. This mold is SiC with 100–200 nm L&S patterns and 150 nm in depth.[5] VUV condition is $T_{\rm sub} = 100°{\rm C}$, $d_{\rm RD} = 3\,{\rm mm}$, $c_{\rm o} = 8\%$, and $P_{\rm VUV} = 10\,{\rm mW/cm^2}$. If considered from the picture of Fig. 5(b), it is enough and succeeded to clean the SiC-mold. However, it remains residual resin in the SEM picture as shown in Fig. 5(c), which is observed in the same sample of Fig. 5(b). It indicates that VUV exposure for 5 minutes is not enough under present VUV exposure conditions. After additional 5 minutes VUV-exposure, the SiC-mold was observed by SEM, and no attached resin was seen on the SiC-mold surface, as shown in Fig. 5(d). In the case of thermal imprint using SiC-mold and PMMA-resin pair, 10 minutes VUV-exposure is very effective for reproduction of contaminated molds.

Figure 6 shows the cleaning result of quartz mold, which contains attached UV resin, TR-21B. The quartz consists of 150–300 nm L&S patterns with depth of ca. 250 nm.[6] The UV-imprint resin is difficult to remove from the quartz-mold by using organic solvents, such as acetone and alcohol, which are generally used to wash out various resins. VUV condition is $T_{\mathrm{sub}} = 25°\mathrm{C}$, $d_{\mathrm{RD}} = 2\,\mathrm{mm}$, $c_{\mathrm{o}} = 20.9\%$, and $P_{\mathrm{VUV}} = 100\,\mathrm{mW/cm^2}$. Figures 6(a), (b), and (c) show pictures of optical microscope taken before VUV exposure, and after 5 and 10 minutes exposure, respectively. Strongly attached UV-imprint resins are removed by 5 minutes VUV-exposure, and residual UV resins in the grooves are completely removed from the quartz-mold as shown in Fig. 6(c). It is difficult to observe quartz by SEM. However, it is obvious that VUV-exposure is very effective for reproduction of quartz-molds too.

4. Conclusion

The cleaning treatment of contaminated resins on the concavoconvex-substrates by exposure of vacuum ultraviolet (VUV) proves very effective not only for the imprint resins but also for various resins. Effective ashing of resins is induced by long time-, high substrate temperature-, and short distance- VUV exposure. In addition, optimum oxygen concentration exists. The cleaning procedures for imprint-molds is successfully established.

Acknowledgments

A part of this research was supported by Grants-in-Aid for Scientific Research, MEXT (No. 20200028) and JST/CREST.

References

1. M. Nakao, Nanoprinting technology, *Trans. Inst. Electron. Inform. Comm. Eng.* **J85-C**(9) (2002) 793–802.
2. S. Y. Chou, P. R. Krauss and P. J. Renstrom, Imprint of sub-25 nm vias and trenches in polymers, *Appl. Phys. Lett.* **67** (1995) 3114–3116.
3. Y. Hirai, K. Kanankugi, T. Yamaguchi, K. Yao, S. Kitagawa and Y. Tnaka, Fine pattern fabrication on glass surface by imprint lithography, *Microelectronic Engineering* **67–68**(1) (2003) 237–244.
4. M. Yamaguchi, T. Wallow, Y. Yamada, R.-H. Kim, J. Kye and H. J. Levinson, A study of photoresist pattern freezing for double imaging using 172 nm VUV flood exposure, *J. Photopolym. Sci. Technol.* **21**(5) (2008) 697–704.
5. S. W. Pang, T. Tamamura, M. Nakao, A. Ozawa and H. Masuda, Direct nano-printing on Al substrate using a SiC mold, *J. Vac. Sci. Technol. B* **16** (1998) 1145–1150.
6. M. Nakao, S. Ishizuka, S. Kataza, S. Shoji, S. Mashiko and J. Mizuno, Batch Fabrication of First-Order Grating for DFB Lasers on 3-inch GaAs Substrates by Using UV-Imprint and Chlorine-ICP-RIE Techniques, *IEEE Nanotechnol. Mat. Devices Conf.* 2008 (NMDC2008), Kyoto (Oct. 20–22, 2008) TuA II-3.