

Chapter 10 Conclusions and Future Outlook

The zwitter-polymer demonstrates the positive tone as the dosage of electron beam is between 3 to 300 $\mu\text{C}/\text{cm}^2$ and the polymer changes into negative tone as the dosage is over 300 $\mu\text{C}/\text{cm}^2$. In the general, the electron beam irradiation occurs the scattering dose due to the elastic and inelastic collision of electron. In this work, the thermal effect of electron beam exposure is found, which results in structural transformation of polymer. The simultaneous demonstration of positive tone and negative tone leads to the formation of a ring pattern. The natural logarithm dependence of ring width and electron beam dose is linear at 300– 550 $\mu\text{C}/\text{cm}^2$ and 600–900 $\mu\text{C}/\text{cm}^2$, respectively. The electron scattering effect controls the resolution as the dosage is below 550 C/cm^2 , while the thermal effect is significantly larger than the scattering effect as the dosage is over 600 $\mu\text{C}/\text{cm}^2$. Taking the electron scattering and electron heating into consideration, a semi-empirical model for prediction of ring width for zwitter-polymer is established. The model demonstrates a very good correlation in comparison with the experimental results obtained from in-line SEM measurements.

Furthermore, the structure of acrylic resin with linear and crosslink can be modified through electron beam irradiation for application of positive tone and negative tone resists. The zwitter-polymer resist exhibits a positive tone when the dosage is in the range 3–300 $\mu\text{C}/\text{cm}^2$, and a negative tone for dosages $> 300 \mu\text{C}/\text{cm}^2$. The contrast ratios for the positive tones are about double those of the negative tones; the significant degradation of contrast ratio for the latter is caused by the higher threshold dose. The vinyl group is produced from the chemical chain scission at low electron dose, resulting in polymerization by following larger dosage. The measured

trench width is equal to that of the designed trench at a dose of $8.5 \mu\text{C}/\text{cm}^2$ for positive tone, and at a dose of $880 \mu\text{C}/\text{cm}^2$ for negative tone. The resolution for zwitter-polymer approaches nanoscale with dense-line and contact hole. The electron beam exposure facilitates etch resistance of the resist in the low-dose region, but higher dose exposure results in the inverse effect.

The other material, epoxy, is used to irradiate by electron beam and compared with PMMA and KrF UV-86 resist. The epoxy demonstrates good performance in patterning oblique structures as a result of its lower contrast, higher throughput, better etching resistance, and excellent thermal properties, relative to the PMMA and KrF UV-86 resists. The initial surface with hydrophobic property becomes hydrophilic after plasma treatment for 20–40 sec, thus hydrophobic character is restored after 50–60 sec of plasma treatment. The formation of surface nodules, as evidenced by SEM, can be used to reasonably explain the transformations in surface hydrophobicity. We have demonstrated a novel gradient writing strategy that uses electron beam exposure to fabricate a sloped structure. The inclined angle of the structure was found to have an inverse relationship with respect to the dose received per unit area. Furthermore, curved devices, such as convex, concave, and spiral structures are fabricated by electron-beam writing strategy. Cross-sectional SEM images clearly indicate that the writing strategy we have proposed can be used successfully to fabricate obliquely patterned structures.

The SAM of fluoroalkyl substituents on silicon oxide surfaces for nanoimprint reduces the physical and chemical adhesion between mold (SiO_2/Si) and resists. The higher fluorosiloxanes with longer flexible chain reduced the roughness of the resists after separation from mold due to the lower mechanical adhesion. The total surface energy decreased with the increase of $-\text{CF}_2$ amount, resulting in the optimum pattern

of isolated trench after separation from mold with FOTS monolayer.

The mold with thermosetting polymer pattern has been fabricated in imprint process, which simplified the etching and resist removing process for mold fabrication. The hill-like structure fabricated by electron beam for thick film prevent the thermosetting polymer patterns lift-off from silicon wafer surface as separation from thermoplastic polymer resists. Two and three dimensional patterns were fabrication by using thermoplastic polymer resist for imprinting by mold with thermosetting polymer patterns. The molds with various 3D microlens were imprinted onto thick thermoplastic polymer resists by a NIL apparatus. As a result, it was confirmed that a 3D mold, after the NIL, kept its original shape, and 3D structures were successfully imprinted onto the thermoplastic polymer resists. The shrink effect was found as the thermosetting polymer patterns separated from thermoplastic polymer resists under the imprint process. Furthermore, a PDMS microlens has been fabricated successfully by using a thermoplastic polymer resists reversal microlens mold.

The future works are focused on electron beam irradiation and nanoimprint technologies. In the case of electron beam technology, the structural transformation of polymer under electron beam irradiation is a critical issue. In the future, we will extend the experiment about the fundamental analysis of structural transformation for various polymers under electron beam irradiation to establish the reaction mechanisms of polymer irradiated by electron beam. In the case of nanoimprint technology, the SAM technique is developed toward bottom-to-up fabrication. We will synthesize the multi-layers film with nanoscale on the silicon wafer through ATRP reaction. The multi-layers film has low surface energy on the surface, while has high adhesion with silicon wafer for nanoimprint technology.

The prospects for nanoimprint-based techniques are wide open. These are based

not only on the low cost of their nanometer-scaled fabrication processes but also on the potentially huge range of applications, mainly at the end of less demanding applications. However, many key issues in NIL machines, masks, resists, and processes still need to be solved. Among some of the issues requiring further investigation and discussion, On the science front, the relative ease of these techniques is bound to make them a common laboratory tool to study surface and interface phenomena, beyond the solid state, by putting within the reach of scientists the use of patterned substrates down to 10 nm for their research. As high-throughput and low cost nanopatterning technologies, NIL will play an important role in future development and manufacturing of nanostructure.



List of Publications

1. **Jem-Kun Chen**, Fu-Hsiang Ko, and Feng-Chih Chang, “Mechanism and Modeling of Ring Pattern Formation for Electron Beam Exposure on Zwitterresist”, **Jpn. J. Appl. Phys.**, 42, 3838-3841 (2003).

2. **Jem-Kun Chen**, Fu-Hsiang Ko, Hsuan-Ko Chen and Cheng-Tung Chou, and Feng-Chih Chang, “Fabrication of Three-dimensional Non-planar Fluidic Channel with Electron Beam Lithography”, **J. Vac. Sci. Technol. B**, 22(2), 492-500 (2004).

3. **Jem-Kun Chen**, Fu-Hsiang Ko, Chia-Hao Chan, Chih-Feng Huang, Chih-Feng Wang and Feng-Chih Chang, “Novel Electron Beam Writing Strategy for Fabrication of Oblique Structures”, **J. Electrochemical Society**, 2004, accepted.



4. **Jem-Kun Chen**, I-Kuang Lin, Fu-Hsiang Ko, Shiao-Wei; Su, Chih-Feng Huang, Kuo-Shen Chen, Chia-Hao Chan and Feng-Chih Chang, “Behavior and Surface Energy of Polybenzoxazine Polymerized by Argon, Oxygen, and Hydrogen Plasma”, **J. Polym. Sci. B**, 2004, in press.

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Chou and Feng-Chih Chang,” Effect of Fluoroalkyl Substituents on the Reaction of Alkylchlorosilanes with Silicon Oxide Surfaces for Nanoimprint”, **J. Vac. Sci. Technol. B**, 2004, accepted.

7. **Jem-Kun Chen**, Fu-Hsiang Ko, Chih-Feng Huang, Kuo-Shen Chen Chih-Feng Wang and Feng-Chih Chang,” Fabrication of Mold with Thermosetting Polymer Pattern through Imprint Technology for Three Dimension Devices”. **J. Electrochemical Society**, submitted.
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9. Chia-Hao Chan, **Jem Kun Chen**, Feng-Chih Chang, “In-Situ characterization of Cu CMP slurry and defect reduction using IR thermal camera”, **Microelectronic Engineering**, 75, 257-262 (2004).
10. Wen Yi Chen, **Jem-Kun Chen**, and Feng-Chih Chang,” Thermal and Dielectric Properties and Curing Kinetic of Nanomaterial Based on Poss-Epoxy with Meta-Phenyldiamine”, **Polymer**, 2004 in press.
11. Lee, Yuan-Jyh; Kuo, Shiao-Wei; Su, Yi-Che; **Chen, Jem-Kun**; Tu, Cheng-Wei; Chang, Feng-Chih, “Syntheses, thermal properties, and phase morphologies of novel benzoxazines functionalized with polyhedral oligomeric silsesquioxane (POSS) nanocomposites”, **Polymer**, 45, 6321 (2004).

12. Yuan-Jyh Lee, Jieh-Ming Huang, Shiao-Wei Kuo, **Jem-Kun Chen**, and Feng-Chih Chang, “Synthesis and Characterizations of a Vinyl-Terminated Benzoxazine Monomer and its Blending with Polyhedral Oligomeric Silsesquioxane (POSS)”, **Polymer**, in submitted.
13. Chih-Feng Huang, Shiao-Wei Kuo, Han-Ching Lin, **Jem-Kun Chen**, Yu-Kai Chen, Hongyao Xu, Feng-Chih Chang,” Thermal properties, miscibility and specific interactions in comparison of linear and star poly(methyl methacrylate) blend with phenolic”, **Polymer**, 45, 5139 (2004).



Introduction to Author

English name: Jem-Kun Chen Chinese name: 陳建光

Sex: male

Birthday: 1973 June 3

Address: No. 92, Chang-Ming Road, Ping-Dong County 920, Taiwan

E-mail address: u810650@alumni.nthu.edu.tw



Education:

B.S., Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan.

M.S., Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan.

Ph.D., Institute of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan.

Experience:

Probationer, Department of Electronic Engineering, Stephen Y. Chou laboratory, Princeton University USA.



Conference:

1. Nanoimprint Processes and Components Session, 48th Electron, Ion and Photo Beam Technology and Nanofabrication (EIPBN), San Diego, California, 201-202 (2004).
2. International Microprocesses and Nanotechnology Conference (MNC), (2003).
3. Nanobiology Session, 47th Electron, Ion and Photo Beam Technology and Nanofabrication (EIPBN), Tampa, FL, 201-202 (2003).
4. International Microprocesses and Nanotechnology Conference (MNC), (2002).
5. 46th EIPBN, Anaheim, CA, 201-202 (2002)