論文 / 著書情報
Article / Book Information

題目(和文)	熱ナノインプリントによる原子スケールで 表面パターン化されたポリマー材料の作製と応用
Title(English)	Thermal nanoimprint fabrication and application of atomically surface-patterned polymer materials
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種別(和文)	論文要旨
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

専攻： Department of	物質科学創造　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（　工学　）
学生氏名： Student's Name	譚　ゴオン	指導教員（主）： Academic Advisor(main)	吉本　護
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In this thesis, the atomic-scale patterning onto various polymer materials by thermal nanoimprint process was achieved by using the atomically stepped sapphire molds. The regularly aligned step patterns (~0.3 nm for step heights and ~800 nm for step separations) were successfully fabricated on the PMMA and polyimide polymer sheets. Large-area transcription was attained on the PMMA surface under the conditions of smaller than 0.2 MPa at 120 °C for 5 min. The RMS roughness of the imprinted PMMA for a 10×10 μm^2 area is approximately 0.19 nm, which is about 10 times smaller than that of the pristine PMMA surface. According to the cross sectional profile, the sapphire mold has regularly arranged atomic steps with a terrace width of 700—800 nm and a uniform height of 0.34 (±0.01) nm. In contrast, the step terrace width and height of imprinted PMMA are 700—800 nm and 0.29 (±0.01) nm respectively, which are close to those of the sapphire mold. This decrease might be caused partly by thermal shrinkage during cooling process or by viscoelastic relaxation of macromolecules owing to the stress induced near the step edges in the molding process. It was also found that the PMMA surface can maintain the atomic-scale steps for over one year. Next, the atomic-scale thermal change of the 0.3nm-high stepped pattern on the PMMA surface was investigated by an in-situ AFM system. In-situ AFM equipped with a heater stage revealed the step pattern formed on the PMMA surface was stable at ~120 °C higher than its bulk glass transition temperature of 105 °C. At higher heating temperature, the step pattern gradually faded away and completely disappeared after heating the AFM stage at 135 °C. Then, the annealing time was investigated to confirm wither the pattern collapse can be assigned to a relaxation process. The annealing temperature was fixed at 125 °C. It was found that the step pattern gradually faded away with prolonging the annealing time and disappeared around 10 minutes. Therefore, it was plausible that the pattern collapse was mainly caused by a relaxation process of PMMA. It seems the pattern collapse is mainly caused by the α-relaxation process of PMMA because other processes (β-, γ- and δ-relaxations) are thought to occur at the lower temperatures. The α-relaxation is related to the long-range conformational changes of the polymer backbone. Therefore, it is suggested that the step structure might be formed by the conformational changes of the polymer backbone. The atomically stepped patterns were also transferred onto the heat-proof polyimide sheets (T_g: ~265 °C). The heat-resistant and transparent polyimide sheets exploited here are expected to be applied toward the flexible polymer substrates for transparent thin film growth. The atomically stepped pattern was transferred onto the polyimide surface with high fidelity under the conditions of smaller than 0.2 MPa at 260 °C for 5 min. The fabrication of ultrasmooth indium tin oxide (ITO) thin films on the imprinted polyimide sheets was also demonstrated. Pulsed laser deposition (PLD) was used to fabricate ITO films under the conditions of 1.3 Pa O_2 atmosphere using a sintered bulk target and a pulsed KrF excimer laser (wavelength: 248 nm, pulse duration: 20 ns, laser fluence: ~1.4 J/cm^2, and frequency: 10 Hz). For the ITO thin film deposited at 200 °C, the ITO surface didn't reflect the step pattern formed on the imprinted polyimide surface. This was probably because of the large migrations of film precursors. The crystalline ITO thin film reflecting the atomically stepped pattern was attained via post-anneal process of 200 °C in vacuum (~10^{-6} Pa) for 1 hour. The RMS surface roughness of ITO film on the patterned polyimide sheet was about 2 times smaller than that on non-patterned one. This indicates the ultrasmooth polymer substrates are expected to be applicable to fabricate nanoscale-controlled electronic devices such as superlattices, nanowires, or quantum dots. The atomically stepped polyimide is also advantageous to the ultrasmooth stage for observing biochemical materials and macromolecules. In order to explore the two-dimensional nanoengineering of polymer surfaces for biological application, nanoscale letter was written on the atomic step-and-terrace polyimide surface via AFM-probe scratching. The AFM-probe scratch was performed in a friction mode. After line-scanning in the friction mode, the surface was observed again in the tapping mode. As a result, the letter "T" with approximately 0.35-nm depth was clearly observed on the flat terrace. The local surface modification might influence chemical or biomolecular attachment and have an application in selective adhesion of molecules on the substrate. In conclusion, thermal nanoimprint process was found to be able to modify polymer surfaces at atomic scale. The atomically stepped pattern with ultrasmooth step terraces is thought to be applied in flexible substrates for electronic thin-film growth and observation of organic molecules. Therefore, the atomic-scale patterning of polymer surfaces shown in this study is expected to open a new field of polymer science and nanotechnology.