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学位授与年月日	平成２９年３月２４日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）応用化学専攻
学位論文題目	Nanometer-Resolved Fluidity of Diacrylate Monomers between Silica Surfaces for Sub-15 nm Ultraviolet Nanoimprinting (サブ 15nm 光ナノインプリント成形に向けた重合性モノマーのシリカナノ空間での流動性)
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論 文 内 容 要 旨

The title of this thesis is “Nanometer-Resolved Fluidity of Diacrylate Monomers between Silica Surfaces for Sub-15 nm Ultraviolet Nanoimprinting”. The author investigated fluidity of diacrylate monomers confined between unmodified and modified silica surfaces for sub-15 nm patterning by UV nanoimprinting. Nanometer-resolved surface characterization methods of surface forces and resonance shear measurements revealed the effects of chemical compositions of surfaces and monomers on fluidity in nano-space. The author provided silica templates with sub-15 nm concave holes by electron beam lithography, and investigated resin filling behavior into the silica recesses by UV nanoimprinting using the templates.

In the first chapter, the author described a background and an objective of this thesis. UV nanoimprint lithography (UV-NIL) is one of promising nanofabrication technologies for forefront semiconductor devices because of its high resolution, high throughput, and low cost. The process comprises the following steps: i) pressing a silica mold with nanostructures onto a UV-curable resin film coated on a substrate, ii) filling the mold recesses with the liquid resin, iii) curing the resin by UV light exposure, iv) releasing the mold, v) removing a residual layer of the pattern with the plasma etching process, vi) etching the substrate by using the residual resin as an etching mask, and vii) removing the residual resin to obtain a substrate pattern. Nanostructures at the mold surface are transferred onto the substrate surface by the one-to-one technique. Several demonstrations of sub-15 nm patterning by UV nanoimprinting have been reported in last two decades, whereas fundamental insights based on surface science and chemistry still remain unclear because the recent developments have been achieved by empirical studies. Prof. Nakagawa’s laboratory has been investigating the process in terms of surface science and chemistry. Carbon-coated anodic aluminum oxide (AAO) films with around 20-nm-diameter holes were provided and used in UV nanoimprinting to investigate resin filling behavior into concave recesses. Analysis of the fabricated pillar patterns of UV cured

resins indicated that the number of pillars increased with an increase of the number of hydroxy groups in a base monomer. It was found that resin filling into concave recesses with around 20-nm-diameter depended on chemical structures of monomers. From this insight, the author determined to investigate the effects of chemical compositions of surfaces and monomers on fluidity of monomers confined in nano-space. It is well known that liquid confined between surfaces shows an increase in viscosity near the interface. The increase in viscosity during UV nanoimprinting would have influences on resin filling, horizontal movement of a mold for alignment, and photopolymerization of monomers in nano-space. The objective of this thesis is to reveal fluidity of diacrylate monomers between silica surfaces and to demonstrate sub-15 nm patterning by UV nanoimprinting.

In the second and third chapters, fluidity of diacrylate monomers between silica surfaces was investigated by surface forces and resonance shear measurements. Diacrylate monomers of 1,10-decanediol diacrylate (AC10), dipropenic acid (1-methyl-1,2-ethandiyl)bis[oxy(2-hydroxy-1,3-propanediyl)] ester (70PA), and glycerol 1,3-diglycerolate diacrylate (GDD) were selected in terms of the chemical compositions; AC10 without hydroxy groups, 70PA with two hydroxy groups, and GDD with three hydroxy groups in a monomer structure. Silica sheets cut from flamed silica tubes and glued on cylindrical silica lenses were prepared for the measurements. Silica surfaces modified with chlorodimethyl(3,3,3-trifluoropropyl)silane (FAS3-Cl) or tridecafluoro-1,1,2,2-tetrahydrooctyltrimethoxysilane (FAS13) by chemical vapor surface modification were molecularly smooth enough to carry out the measurements. The FAS3-Cl-modified and FAS13-modified silica surfaces and unmodified silica surfaces treated by vacuum UV light exposure were used for the measurements. The silica sheets glued on silica lenses were mounted on the setup with the cylindrical surfaces faced perpendicularly. The liquid monomer was inserted between the surfaces. The distance (D) between two silica surfaces was determined using fringes of equal chromatic order (FECO) generated by interference of white light between the silver layers deposited on the backside of the silica sheets. We defined the surface distance $D = 0$ for the fluorinated silica surfaces as the contacting probe surfaces in air after surface modification. The surface forces and resonance intensities as a function of the angular frequency were measured upon stepwisely decreasing D and plotted as surface forces curves and resonance curves, respectively. The obtained resonance curves were analyzed using a physical model and viscous parameters b_2 were calculated. The b_2 value of AC10 between unmodified silica surfaces began to increase at $D = 6$ nm and steeply increased at $D < 4$ nm, indicating structuring of monomers confined in nano-space. FAS3-Cl-modified and FAS13-modified silica surfaces increased b_2 values at shorter D than that between unmodified silica surfaces, indicating that the monolayers suppressed the monomer structuring near the interfaces due to weakened intermolecular interactions of monomers and the surfaces. The D between FAS13-modified silica surfaces jumped into contact named as "jump-in" phenomenon in the field of surface forces measurements. It was suggested that FAS13-modified silica surfaces caused thermodynamic instability of monomers confined in sub-10 nm space. These

results were consistent with surface forces measurements. The b_2 values of AC10, 70PA, and GDD monomers between unmodified silica surfaces were displayed in the same axis to compare the difference in b_2 values of the monomers. Intriguingly, the b_2 values at $D < 5$ nm and at hard wall showed reverse order in comparison with b_2 in bulk state. This result indicated that hard-wall structuring showed opposite tendency from fluidic structuring. In these chapters, it was revealed that nanometer-resolved fluidity of liquid monomers depended on the interactions of monomers with surfaces.

In the fourth chapter, the fabrication of silica templates with sub-15 nm concave holes was investigated using electron beam lithography (EBL) involving Ar ion milling. The etching rate of a positive-tone EB resist film in Ar ion beam milling was consistent with the one of a silica substrate. The identical etching rates of the EB resist and silica motivated the author to use the resist layer as an etching mask to silica surfaces. Concave hole patterns on an EB resist film were fabricated by EB spot drawing and subsequent developing. Hole patterns with a diameter of sub-15 nm were observed on the film by field-emission scanning electron microscopy (FE-SEM). The concave patterns were transferred onto a Cr/silica substrate by Ar ion beam milling. Sub-20 nm holes were fabricated, while non-etched defects were generated here and there in the region with a hole diameter of 10 nm. Because the Ar ion beam milling has less anisotropy in etching, we think that Ar ion species has more difficulty to reach to bottom surfaces in the resist holes with a diameter of 10 nm and height of 40 nm. Therefore, the author further investigated how to fabricate silica templates with hole diameters from single digit nanometers by combining Ar ion milling and inductively coupled plasma (ICP) etching. The cross-sectional FE-SEM images showed the vertical concave holes on a silica template. The hole diameters were 20, 15, and 7 nm. Concave holes with sub-15 nm features were fabricated by EBL using Ar ion milling and ICP etching. UV nanoimprinting using the silica template was carried out and the transferred patterns were observed by atomic force microscopy (AFM). Topographic images showed pillar patterns of AC10-based cured resins fabricated using the FAS13-modified silica template. The fabrication of sub-15 nm pillar-like structures were demonstrated, whereas heights of the structures were lower in comparison with hole depths on a silica template.

In the fifth chapter, newly synthesized silicon-containing (meth)acrylates were designed and added into a UV-curable resin to enhance the etching durability to O_2 reactive ion etching (O_2 RIE) for removing a residual layer. The additives were newly designed and synthesized by collaborators because the presence of the phenyl group increases the value of the ring parameter of cured resins and because inorganic silica species generated by the oxidation of such silicon-containing compounds during O_2 RIE improves etching durability. The addition of the additives decreased the etching rate of UV cured films from 42.0 nm min^{-1} to 26.8 nm min^{-1}. The addition of the additives to the base resin improved etching durability to O_2 RIE. Line patterns with a width of 45 nm were fabricated by UV nanoimprinting using the resins without and with the additives. Line breaks and fusion were observed everywhere for imprint patterns made from the resin without additives. It was difficult to maintain line-and-space patterns after O_2 RIE owing to the low etching durability. In contrast, line-and-space imprint patterns remained

on a silicon wafer after O_2 RIE in the case of using the resin with additives. It was found that the silicon-containing additives effectively improved etching durability to O_2 RIE for the removal of a residual layer generated after imprinting. However, some line break defects still remained, and the line edge roughness of the resist patterns increased after O_2 RIE. For sub-15 nm UV-NIL, it is necessary to further study how to reduce the line break defects and to maintain the line edge roughness after O_2 RIE. The author proposes that a resin with silicon-containing additives would be available as an etching mask for reverse-tone UV nanoimprinting.

In this thesis, the nano-rheological properties of diacrylate monomers between fluorinated silica surfaces were evaluated for sub-15 nm patterning by UV nanoimprinting. Sub-15 nm patterning using a silica template with concave holes fabricated by EB lithography was demonstrated, and the resin filling behavior into sub-15 nm silica recesses was discussed considering the nanometer-resolved fluidity of monomers. For sub-15 nm patterning by UV-NIL, the etching durability of UV cured resin films was enhanced by adding silicon-containing additives for etching a residual layer in O_2 RIE with maintaining the pattern size. This thesis provides fundamental insights into the viscosity increases derived from the chemical interactions of the surfaces and monomers and those from among the monomers. The evaluation of the nanometer-resolved fluidity of monomers between unmodified and modified silica surfaces was established, and sub-15 nm patterning, to investigate resin filling into sub-15 nm silica recesses, was demonstrated using a silica template with concave holes fabricated by EBL. The author anticipates that the increase in the monomer viscosity under confinement would affect the fabrication of smaller patterns with sub-15 nm and forefront sub-7 nm features by UV-NIL because the viscosity increase would cause non-fill defects in the mold recesses, a difficulty in moving a mold horizontally for alignment, insufficient curing of resins in the mold recesses, and pull-out defects arising from insufficient curing. To decrease the viscosity confined between the nanospace would be important for sub-15 nm and forefront sub-7 nm patterning by UV nanoimprinting. Further investigation of the nano-rheological properties of UV-curable resins confined between identical and different surfaces are required to overcome the challenge to decrease the viscosity under confinement. The obtained insights reported in this thesis should be helpful for the fabrication of sub-15 nm and sub-7 nm patterns on semiconductor devices to be used by the “big-data society” and in the “Internet-of-Things”.

論文審査結果の要旨

光ナノインプリントリソグラフィ（UV-NIL）は簡便、かつ低コストで高精度のナノ構造体を量産可能であることから、サブ15nmスケールの次世代半導体デバイス作製技術として期待されている。ナノサイズの凹凸構造を有する鋳型（モールド）を液状の紫外線硬化性組成物に押し付けた後、紫外線照射により液体を硬化させ、鋳型を離型することでナノパターンを転写する。サブ15nm空間中での液体の流動性や光ナノインプリントによる定量的な報告は未だ僅少であり、実学応用にはサブ15nm成形に向けた学術的知見が不足している。本論文は、サブ15nm成形に向けた光重合性モノマーのシリカナノ空間中での流動性を界面分子科学に基づく実験的手法から定量的に解明している。作製したナノ構造体を有するモールドを用いてサブ15nm成形を実証し、モノマーのナノ流動性が表面と液体の化学組成によって変化することを見出している。本論文は全六章から成る。

第一章は序論であり、本研究の背景及び目的が述べられている。

第二章では、表面力測定装置を用いて液体モノマーを介したシリカ表面間で生じる表面間力をナノスケールで評価している。まず、ナノ分解能の測定が可能なシリカ表面のフッ素修飾方法を確立している。長鎖フルオロアルキルのFAS13修飾シリカ表面間では親油性モノマーは表面誘起相分離により9nm以下のナノ空間から押し出されることが示された。一方、親水性モノマーは水素結合による強い分子間力により9nm以下のナノ空間でも安定した層を形成することが明らかとなった。光重合性モノマーを介したシリカ表面間に生じるナノ分解能での表面力測定を示した有益な報告である。

第三章では、共振ずり測定によりシリカナノ空間での液体モノマーの流動性を評価している。液体モノマーの粘度が20nm以下のナノ空間中で増大すること、親水性モノマーに比べて親油性モノマーの方が粘度の増加し始める距離が小さいことが示されている。シリカ表面のフッ素修飾によりナノ空間中での粘度上昇が抑制できることが明示されている。また、異なる粘度のモノマーの測定から、5nmより小さい空間中では粘度の大小がバルク粘度の順番と逆転することを明らかにしている。ナノ空間中でのモノマー粘度の測定手法の確立と、サブ15nm光ナノインプリントに向けたモノマー・表面の化学組成設計に指針を与えることができる、極めて有益な成果である。

第四章では、電子線リソグラフィ（EBL）によるサブ15nmホール構造を有するシリカモールドの作製とサブ15nm光ナノインプリント成形の実証が示されている。サブ15nm凹構造を有するシリカモールドを作製するためのEBLに関する手法が述べられている。第二章、第三章にて得られたモノマーのナノ空間中での流動性を基に、7nmでの成形を実証し、実際の光ナノインプリントプロセスにおけるモノマーの充填挙動について議論している。サブ15nm構造体を有するシリカモールド作製は有益な成果であるとともに、サブ15nmにおける充填挙動について化学的観点から議論がなされており、材料開発と表面設計における非常に有益な指針が示されている。

第五章では、UV-NILにおける光硬化樹脂のエッチング耐性増加に向けたシリコン含有添加剤の導入を提案している。添加剤含有光硬化樹脂は優れたエッチング耐性を示した。ラインパターンにおけるエッチング耐性と添加剤の有用性が論述されている。未だ課題が残るが、UV-NILによる基板加工に向けた優れた提案が行われている。

以上、本論文では、シリカナノ空間中での液体モノマーの流動性が解明され、その知見に基づいたサブ15nm成形に成功している。サブ15nmスケールのUV-NILの実用化に向けたナノ空間中でも高い流動性を示す材料開発に対する指針が明示されており、本論文が工学的に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。