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Planarization of polymer materials using catalytic reaction in pure water

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Abstract
In recent years, polymer materials with excellent properties, such as chemical resistance, heat resistance, and high insulation, have been produced. These materials have been widely used in advanced devices. For example, polycarbonate (PC), polymethyl methacrylate (PMMA), and polyimide (PI) are used as insulating films in microelectromechanical systems (MEMSs), and polytetrafluoroethylene (PTFE) is a promising substrate for next-generation high-frequency devices exceeding 5G. To exploit the excellent properties of these polymer materials, well-ordered surfaces are required. However, because polymer materials are extremely soft, conventional polishing methods that use abrasives cannot produce a damage-free surface. We present an abrasive-free polishing technique called catalyst-referred etching (CARE). In this method, the top surface of the workpiece is preferentially removed via an indirect hydrolysis reaction promoted by a metal catalyst. The surfaces of the amorphous and single-crystalline samples processed using CARE exhibited atomic flatness. We discuss the polishing characteristics and material removal mechanisms of polymers in CARE. The PC and PMMA were polished using Pt and pure water as the catalyst and etchant, respectively. An atomically smooth surface, which could not be fabricated by mechanical polishing, was obtained. Based on observations of the surface, the removal mechanism was estimated as follows. Molecule chains entangle to form clusters that constitute the surface of the polymer and determine the surface roughness. In CARE, the top of this cluster was selectively removed, forming a flat surface similar to that obtained on a single-crystalline polymer material. Therefore, CARE is a promising polishing method for polymer materials.

Polymer materials, polishing, chemical wet etching

1. Introduction

Polymer materials are widely used in various advanced devices because of their chemical stability, heat resistance, and high insulation properties. For example, polycarbonate (PC), polymethyl methacrylate (PMMA), and polyimide (PI) are used as insulating films in microelectromechanical systems (MEMSs), and polytetrafluoroethylene (PTFE) is a promising substrate for next-generation high-frequency devices exceeding 5G [1-3]. To exploit these properties, a high-precision flat surface is required. However, because the surface of polymer materials is extremely soft, many scratches are introduced on the surface of the material by conventional polishing techniques that use abrasives.

We proposed using an abrasive-free polishing technique called catalyst-referred etching (CARE) for atomic planarization of a polymer material that is based on chemical wet etching assisted by a metal catalyst [4]. A conceptual diagram of the CARE is shown in Fig. 1. A polishing pad with a thin metal catalyst layer was used in CARE. The sample and polishing pad were pushed against each other in pure water while rotating. The topmost site of the sample surface, which is frequently in contact with the catalyst layer, was preferentially removed by a catalytic reaction. We have previously reported the fabrication of an atomically smooth surface by CARE using Pt and pure water on a functional material such as SiC and GaN [5, 6]. Each surface has a step-terrace structure with a height of one atomic layer. These results indicate that the step edge atom was preferentially removed, resulting in step-flow etching.

CARE is a promising technique for the atomic-order planarization of polymer materials because it is abrasive-free.

However, from the viewpoint of the material structure, the etching mechanism is considered to be very different from that of a single crystal, which we have already clarified. In this paper, we describe the possibility of an atomic planarization of polymer materials using CARE and discuss the etching mechanism.

2. Experimental method

PC and PMMA, which are highly versatile polymer materials, were prepared as the samples. Fig. 2 shows the schematic of the CARE apparatus. The sample substrate was placed in a holder and pressed onto a polishing pad. The sample and pad rotated independently around each axis. Pt and pure water were used as the catalyst and etchant, respectively. The processing pressure and time were 10 kPa and 1 h, respectively. The processed surface was observed using a white light interference microscope (ZYGO NewView200 HCR) and an atomic force microscope (AFM; SHIMADZU 9700HT).

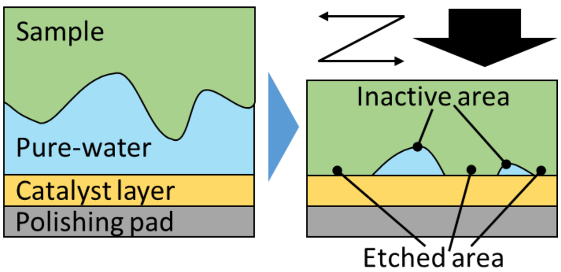

Figure 1. A conceptual diagram of the CARE

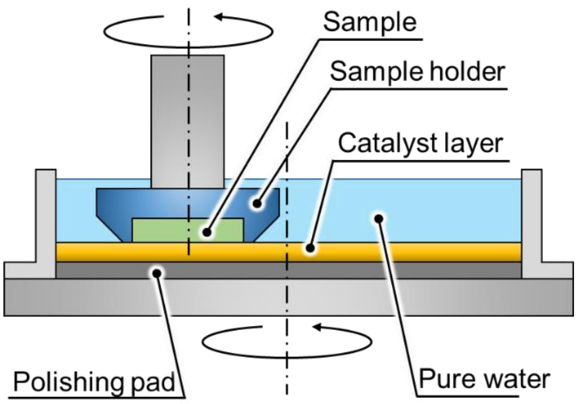

Figure 2. Schematic of the CARE apparatus

3. Result and discussion

Fig. 3 shows the white-light interferometric images of the PC and PMMA surfaces. Figs. 3 (a) and (b) show the as-received surfaces, and Figs. 3 (c) and (d) show the surfaces processed by mechanical polishing with silica abrasive. After mechanical polishing, several scratches were introduced. In the case of using CARE, the surface roughness of PC and PMMA drastically decreased to 1.609 nm and 0.702 nm, respectively, leading to high-precision flat surfaces without scratches, as shown in Figs. 3 (e) and (f). Such a flat surface wasn't obtained without Pt catalyst.

AFM images of the PC surface before and after applying CARE and the cross-sectional profiles are presented in Fig. 4. Notably, the convex part with about 3 nm height was removed from the topmost site owing to the progress of chemical reaction. Although the number of atoms removed at once in an etching reaction is not clear from the AFM image, it is expected that at least a few monomers are removed chemically.

These results indicate that in the CARE process, the polymer material surface was removed by chemical etching, as well as crystalline materials, leading to an ultra-smooth surface without any mechanical damage.

4. Summary

In this study, we proposed the use of CARE, which is an abrasive-free polishing technique, for the planarization of PC and PMMA. The surface roughness was significantly improved, and a smooth surface without any mechanical damage was obtained. AFM observation indicated that the topmost site was preferentially removed by chemical etching with a few monomers. The results show that the CARE enables the realization of atomically flat polymer surfaces that cannot be achieved by the latest polishing techniques. The polymer material treated with CARE improves the performance of various devices.

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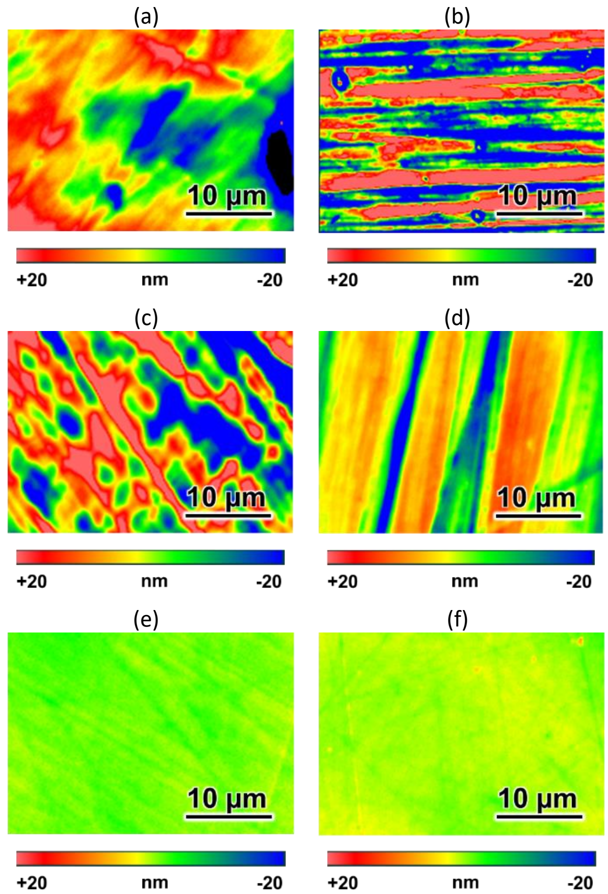

Figure 3. White-light interferometric images of PC and PMMA surfaces. As-received surfaces of (a) PC (rms 15.103 nm) and (b) PMMA (rms 23.259 nm). Silica abrasive polished surfaces of (c) PC (rms 17.354 nm) and (d) PMMA (rms 9.588 nm). CARE polished surfaces of (e) PC (rms 1.609 nm) and (f) PMMA (rms 0.702 nm).

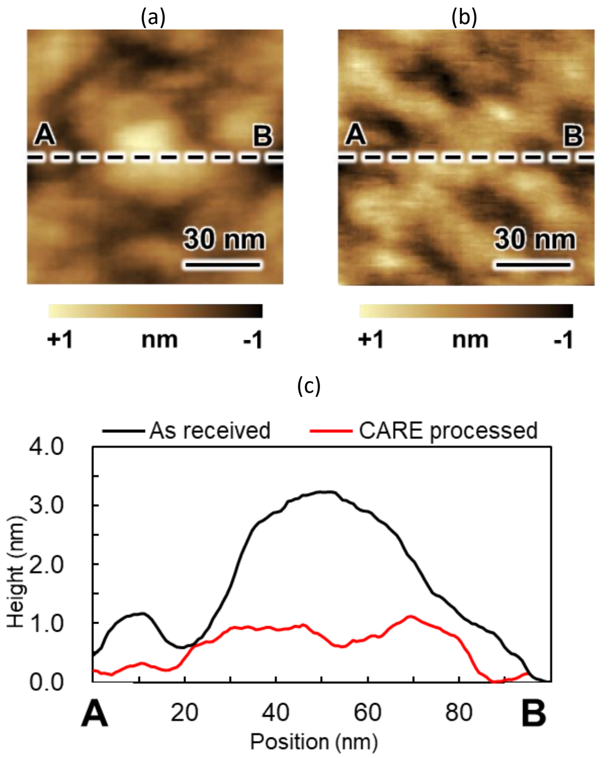

Figure 4. AFM images of the PC surface (a) before and (b) after CARE. (c) The summary of cross-sectional profile of A to B shown in (a) and (b)