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Direct Polymerization of Poly(acrylic acid) on a Silicon-wafer Surface

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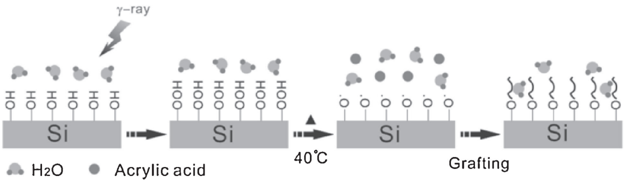
This study examines the direct preparation of poly(acrylic acid) (PAA) on a silicon wafer modified by γ-ray radiation. Using this innovative method, we synthesized PAA on a silicon wafer without additive material because the silicon-wafer itself acts as an initiator. The reaction time was adjusted to control the thickness of PAA on the silicon wafer.

The generation of molecular layers on silicon has been creating increased interest in the field of surface nanostructuring due to its technological applications in areas such as biomaterials, microelectronics, and medicine.[1] Molecular layer grafting on silicon wafers is an important technique that can be used to control the chemical, physical, and electronic properties of a surface.[2] A silicon surface coated with polymer layers appears to be particularly suited to applications requiring versatility and biocompatibility, due to a number of chemical functionalities.

Poly(acrylic acid) (PAA) is a well-known biocompatible polymer used as a polyelectrolyte in various biomedical applications.[3] Previously, Barroso-Bujans et al. studied the grafting of PAA onto an aluminum surface by in situ polymerization (using benzoyl peroxide and 2,2′-azobisisobutyronitrile (AIBN) initiators) and chemical vapor deposition. They compared two methods developed to obtain thin polymer films on metallic substrates.[4] However, the methods are complicated by their need for the formation of an anchorage group. Therefore, we suggest a simpler and more direct polymerization method for silicon wafers that uses γ-ray irradiation. Here we present new procedures for preparing PAA on silicon wafers without an initiator. This method enables control of the PAA thickness, and we were even able to make a gel structure out of a silicon wafer.

First, we prepared 2 cm × 2 cm silicon wafers. Silicon wafers (p-type, surface-polished, back side-lapped, and etched) were used in all of the experiments. The silicon wafers were illuminated with UV light (254 nm, 30 min) to remove a variety of contaminants from the surface and to modify the surface to contain silanol groups using UVO-cleaner.[5] The silicon wafers with silanol groups were irradiated with ^{60}Co γ-rays (dose rate: 10 kGy h^{-1}) at KAERI, Jeongeup, Korea, under ambient conditions for 2 h to create peroxides on the surface.[6] The formation of peroxides on the silicon surface was confirmed by iodometry by using KI.[7] The wafers were then treated with acrylic acid (AA) (98%, Junsei) and placed in an oven heated to 40 °C. The peroxides on the silicon wafers decomposed to oxyl radicals, which acted as initiators at 40 °C. These oxyl radicals initiate grafting polymerization on the silicon wafer with acrylic acid. The mechanism for peroxide formation and the polymerization process on the silicon-wafer surface is described in Scheme 1. We added 5 mL of acrylic acid to 5 mL of water in a 60 mL vial with a diameter of 1.5 cm.



Scheme 1. Mechanism of polymerization on the silicon-wafer surface.

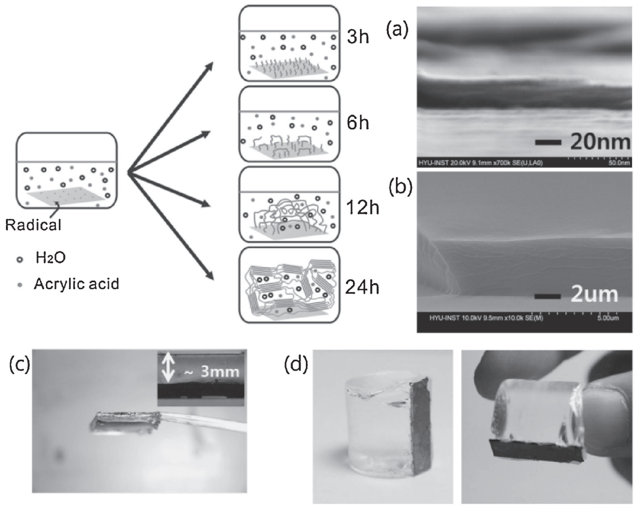


Figure 1. Thickness change of PAA on the silicon wafer with reaction times of (a) 3, (b) 6, and (c) 12 h. The thicknesses were ca. 20 nm, ca. 3 µm, and ca. 3 mm, respectively. (d) is a bulk gel structure after 24 h.

There are several factors that control the thickness of PAA on the silicon wafer, such as the amount of initiator, the total solution volume, and reaction time. All of these factors, except for reaction time, were fixed in our experiment. Silicon wafers irradiated by γ-rays were place in an oven for 3, 6, 12, and 24 h. The thickness increased as reaction time increased, and a gel structure formed after 24 h. Oxyl radicals on the silicon wafers reacted with the acrylic acid monomer as initiators, then grafted onto the silicon wafer surfaces. After 3 h, the thickness of the PAA on the silicon wafer was about 20 nm. As polymer chain lengths grow, they get tangled, and the thickness increases. The PAA layer was 3 µm after 12 h. The thicknesses were confirmed by scanning electron microscopy (SEM) (JEOL, JSM-840A) as presented in Figures 1a and 1b.

Figure 2 shows C(1s) X-ray photoelectron spectroscopy (XPS) spectra of the PAA grafted onto a silicon wafer for 3 h. The C(1s) peak assignment was discussed by Barroso-Bujans et al.[4] The binding energies (BE) were referenced to the C(1s) peak at 284.9 eV.

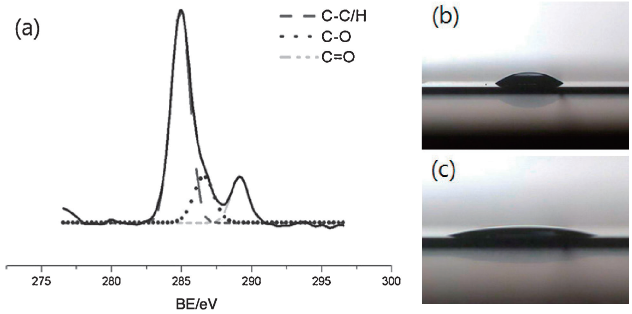


Figure 2. (a) X-ray photoelectron spectroscopy of PAA coated about 3-nm-thick onto silicon wafers; (b and c) contact angle of water on silicon wafers: (b) bare silicon wafer and (c) coated with PAA over 3 h.

The polymer-modified surfaces exhibited three peaks from 280 to 290 eV. The most intense peak, at 285.0 eV, is assigned to C–C and C–H bonds (dashed line),[8] and the less intense peak, at 286.7 eV, is often assigned to C–OH (dotted line). A third peak, at 289.0 eV (dash-dotted line), arises from the C=O groups of PAA.[9] This spectrum suggests the presence of PAA on the silicon wafer. The contact angle measurements clearly show that the surface properties changed dramatically. The water contact angle was high for the bare silicon wafer (37.2°).

In contrast, the silicon wafer coated with acrylic acid monomer over 3 h had a reduced water contact angle value (16.2°) due to the carboxy group from the PAA chain. The interaction between the hydroxy group and the water molecules reduces the surface energy of the silicon wafer.

The polymerization of PAA onto the silicon wafer was confirmed by Raman spectroscopy, carried out with the wide area illumination (WAI) scheme developed by Kaiser Optical Systems (Ann Arbor, MI, USA).[10] The output of the excitation laser (785 nm, diode laser) was magnified to form a circular illumination area with a diameter of 6 mm (area 28.3 mm^2) in order to cover a large sample area. The scattered radiation was then collected by an array of 50 optical fibers and delivered to the charge-coupled device (CCD) detector (Kaiser Raman Rxn1 unit; Kaiser Optical Systems, Ann Arbor, MI, USA). The radiation from the optical fibers was dispersed via a holographic transmission grating. Then a combined signal was integrated over the total illuminated area.

Figure 3 presents Raman spectra of the PAA synthesized on silicon wafers over 6, 12, and 24 h reaction times. The sample with a 6 h reaction time (dotted line) is presented in Figure 1b; its thickness is 3 μm and it shows a very weak Raman reflection signal. It is too hard to detect the Raman signal of a thin layer of PAA on a silicon wafer using the WAI system due to the small amount of polymer molecules. Therefore the dotted line only shows a weak carboxy group peak at 855 cm^{-1}. The sample with a 12 h reaction time (solid line) had PAA and acrylic acid monomer peaks in the Raman spectra. The photograph in Figure 1c is the sample subjected to a 12 h reaction time and Figure 1d is a bulk gel structure after 24 h. The thickness becomes about 3 mm, and the inner image was taken by optical microscopy. The sample contained some water and there was some acrylic acid monomer inside the polymer chain. The peak at 1635 cm^{-1} reflects the C=C stretching mode, and the one at 1290 cm^{-1} reflects the CH_2 twisting mode of acrylic acid. That is, the unreacted monomer captured between the polymer chains when the polymers were grafting onto the silicon wafer. The other peaks in the range from 900 to 1800 cm^{-1} are CH_2 rocking (1006 cm^{-1}), C–CH_2 stretching (1071 cm^{-1}), CH_2 twisting (1284 cm^{-1}), and CH_2 bending (1464 cm^{-1}), which all are due to the presence of PAA.[7] The C–COOH stretching band appears at 855 cm^{-1}, and the C=O stretching mode centers near 1720 cm^{-1} and spans from 1660 to 1760 cm^{-1}. The peak at 1720 cm^{-1} corresponds to the C=O stretching mode of free COOH. The 12 h reaction sample had free volume between the polymer chains due to the other molecules, such as acrylic acid and H_2O. Thus the carboxy groups were able to vibrate freely, causing the peak to appear near 1720 cm^{-1}.

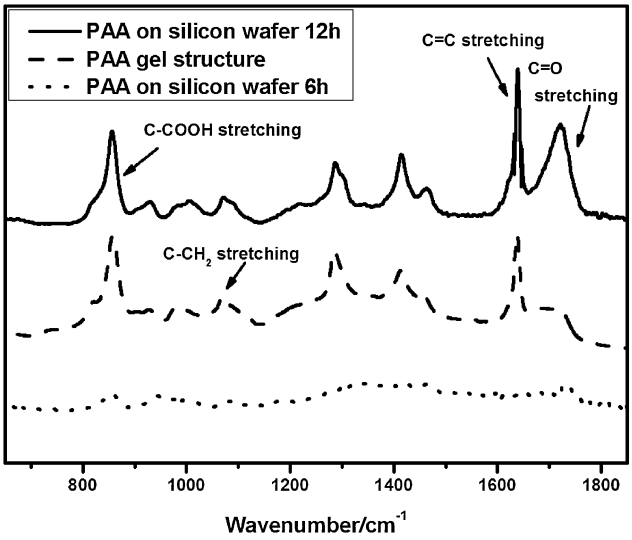


Figure 3. Raman spectrum of PAA coated on silicon wafers over various reaction times. The solid line is the 12-h reaction, the dashed line is the gel-type structure, and the dotted line is the 6-h reaction.

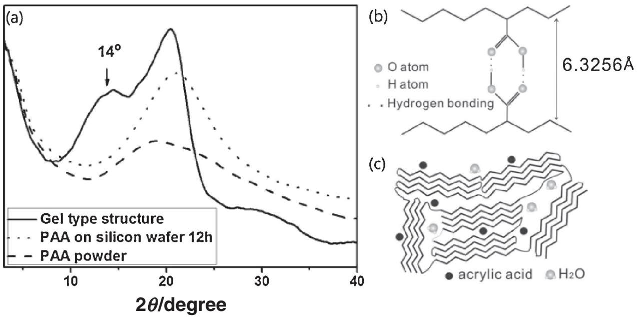


Figure 4. (a) X-ray diffraction pattern of PAA coated on a silicon wafer (dotted line), a gel type structure (solid line), and PAA powder purchased from Aldrich (dashed line); (b) dimer form model of acrylic acid with a 6.33 Å *d*-space; (c) crosslinking model of the dimer crystal region.

The gel structure generated after a longer reaction time was different. The hydrogen bonds between the carboxylic groups of acrylic acid have long been investigated, and it is well known that cyclic dimers exist mainly in the liquid state. Cyclic dimers, as presented in Figure 4b, comprised the crystal region in the gel structure. The carboxy groups of the main chain were fixed by a self-assembled crystal region, which make free stretching of the carboxy groups difficult. That is why the dashed line shows a shoulder peak near 1720 cm^{-1} in Figure 3. This result also corresponds to the X-ray pattern.

The gel structure was further investigated by X-ray diffraction (XRD) using Cu Kα radiation ($\lambda = 1.54$ Å). Figure 4a shows typical XRD patterns of the PAA powder purchased from Aldrich (dashed line), PAA-coated silicon wafers subjected to a reaction time of 12 h (dotted line), and the gel-type structure that resulted from a reaction time of 24 h (solid line). The coated PAA and powdered PAA had amorphous structures with only one very broad peak around 20°. However, there is one more peak around 14° corresponding to 6.325 Å which is the same length scale of the crystals of acrylic acid in orthorhombic with 8 molecules per unit cell. The molecules are planar hydrogen-bonded dimers as presented in Figure 4b.[11] Figure 4c is a crosslinking model of the dimer crystal region.

In conclusion, we developed an innovative method for grafting polymers onto silicon wafers in which the silicon wafer acts as its own initiator. Modified silicon wafers have peroxide groups generated by γ-ray radiation and react with monomers having vinyl groups, such as acrylic acid, without any additional initiator. We controlled the thickness of PAA on the silicon wafer by adjusting the polymerization time. We look forward to controlling growth factors to yield thicknesses ranging from 20 nm to 3 mm and to make a pure acrylic acid gel. In our experiment, polymerization occurred directly on the silicon wafers, enabling more facile grafting onto silicon wafers compared to previous methods.[4] At the beginning, the polymerization occurs by oxyl radicals on the silicon surface. And some radicals on the acrylic acid molecule are released in a solution; it initiates the other monomers and generated the homopolymers. They grow and get tangled with each other, so the thickness increases. An additional initiator is not required because the silicon wafer acts itself as an initiator, which makes grafting PAA nontoxic. Therefore, this study could serve as the basis for developing the simplest methodology for obtaining thin polymer films on solid substrates.

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