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Full Length Article

Design of thermally stable insulation film by radical grafting poly (methylacrylic acid) on silicon surface

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ABSTRACT

The surface modification of silicon (Si) by polymer has great values for insulation film in microelectronics. Necessarily, the polymer film should be thermally stable to withstand the temperature in packaging process. Herein, we report a thermally stable structure of aromatic amide rings by heat treating the radical grafted poly (methylacrylic acid) (PMAA) film. The initiator, 4-Nitrobenzene diazonium tetrafluoroborate (NBD), can provide $-NH_2$ groups (reduced by $-NO_2$ groups) in the polymer film. Dehydration reaction happens between −COOH groups (from PMAA) and $-NH_2$ groups at 200 °C. The products are intramolecular or intermolecular amide rings on benzene ring, with the wettability changing from hydrophilic to hydrophobic. The new structure shows excellent thermal stability after heat treating and the heat-resisting index can be up to 226.6 °C. In addition, the polymer film shows the similar dielectric properties with SiO_2 that could be used as a refined insulation film in microelectronics or semiconductor industry.

1. Introduction

Modern microelectronic devices are directly manufactured on silicon (Si) wafer to improve the integration, which demands for refined insulation film with nanoscale precision. Many grafting methods like ATRP [1,2], ROMP [3,4], RAFT [5,6] and electrografting [7,8] have been intensely studied to achieve the modification of organic film on Si surface. The grafted polymer film with molecular precision bonds to the Si surface through a strong covalent bond (Si−C, or Si−O). Thermal stability of the insulation film is also an important consideration because the film must withstand the temperature in packaging [9,10]. However, until now, the grafted polymer films are usually linear or comb-shaped, which are not benefit for their thermal stability.

The thermal stability of a polymer film is mainly influenced by its structure. As for many polymer structures with excellent thermal stability, rings and cross-linked structures often play an important role. Electrografting of poly-4-vinylpyridine (P4VP) initiated by aryl diazonium salts in aqueous media has shown excellent thermal stability for electrical insulation on Si surface [11,12]. Plenty of phenyl groups (by aryl diazonium salt) and pyridine groups (by P4VP) provide a lot of rings in the polymer film, which is benefit for the thermal stability. (Meth)acrylic derivatives have been widely studied in modification of Si surface, but the molecule chains of the poly((meth)acrylic derivatives) provide no thermally stable structure. To improve the thermal stability, introducing rings or cross-linked structures in the polymer film will be effective.

As reported previously, the connection of aromatic rings and amide bonds could offer excellent thermal stability and mechanical properties [13,14]. Dehydration between amine groups ($-NH_2$) and carboxyl groups (−COOH) could lead to amide bonds [15–17]. Some researchers have found that some nitro groups are reduced to aniline groups ($-NH_2$ groups on aromatic ring) in the process of grafting aryl diazonium salts [18–20]. Methylacrylic acid (MAA) is suitable to provide −COOH groups, which can be grafted onto Si surface by aryl diazonium salts. Thus, the production of dehydrated aromatic amide rings can be achieved by heating the polymer film containing aniline and −COOH groups. In a polymer film, the dehydrated aromatic amide is an intramolecular ring or an intermolecular cross-linked structure, which have high thermal stability.

Herein, we provide a report on fabricating insulation film with ring and cross-linked structures by radical grafting of nitrophenyl and poly (methylacrylic acid) (PMAA) on Si surface. The original organic film is prepared using a reported one-step dipping method. A mechanism is proposed to explain the production of $-NH_2$ groups during the radical

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grafting process. Cross-linking and cyclization of polymer chains are obtained via a traditional heating method. In this process, −COOH groups and $-NH_2$ groups are dehydrated to form aromatic amide structures. The new structure improves the thermal stability of the polymer film that can withstand 200 °C heating for several hours and the heat-resisting index can be up to 226.6 °C. Moreover, the unique structure of thermally stable insulation film with nanoscale precision also provides guidance for other organic polymer films.

2. Experimental section

2.1. Materials

The following reagents were used as received: 4-Nitrobenzene diazonium tetrafluoroborate (NBD, TCI, 97%); methylacrylic acid (MAA, Sinopharm Chemical, 99%); sodium dodecyl sulfate (SDS, Sinopharm Chemical, 98.5%); fluoroboric acid (HBF_4, Sinopharm Chemical, 40%); hydrofluoric acid (HF, Sinopharm Chemical, 40%); ethanol (Sinopharm Chemical, 99%); acetone (Sinopharm Chemical, 99%); calcium hydroxide ($Ca(OH)_2$, Sinopharm Chemical, 80%); deionized water (Milli-Q water). Single-polished Si (1 0 0): p-type, B-doped, resistivity 0.01–0.05 Ω·cm.

The Si substrate was cut into pieces with size of 1 × 2.5 cm^2. Then, Si pieces were ultrasonically washed in acetone, ethyl alcohol and deionized water for 5 min, respectively. Before grafting, the substrate was chemically etched in a HF aqueous solution (3% v/v) over 2 mins to get uniform hydride-terminated Si surface [21].

2.2. Grafting and heating process

The radical grafting of polymer film was described in Ref. [18]. Basically, the polymer film was obtained by one-step dipping method at 20 °C. First, 50 mL of deionized water, 1 mL of HBF_4, 0.5 mL of HF and 2 mL of MAA were added in a 100-mL Teflon beaker. Next, SDS (0.1 g) and NBD (0.15 g) were added. SDS could help reducing the surface roughness of the grafted film. The mixture was then magnetically stirred for several mins until the solution is clear. Finally, Si substrate was dipped into the aqueous solution for 30 mins and then the polymer film was obtained.

The heat treatment of the polymer film was carried out in a tube furnace at two different temperatures, 200 °C and 300 °C, for 1 h with a same heating rate of 5 °C/min, followed by furnace cooling to room temperature.

2.3. Characterization

Surface morphology was studied by scanning electron microscope (SEM, FEI Sirion 200) operated at 5 kV in ultra high resolution (UHR) mode. The surface analysis was also examined by atomic force microscope (AFM, Dimension Icon & FastScan Bio) operated in the PeakForce QNM mode. The film thickness and dielectric properties were measured with a variable-angle spectroscopic ellipsometer (VASE, W-VASE with Auto Retarder TM). The chemical composition was tested by attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR, Nicolet iN MX) with a resolution of 4 cm^{-1} and 64 lines. The chemical structure was also studied by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra). Photoelectrons were stimulated by Al Kα source and operated at 75 W. The data were calibrated by C 1s at 284.8 eV. Contact angles (CAs) were measured by an optical contact angle meter (Data physics OCA20) with a 4 μL water droplet. Thermogravimetric analysis (TGA, Pyris 1 TGA) was tested from 30 to 600 °C with the heating rate of 5 °C/min. The polymer was collected and washed from the grafting solution by centrifugation with the speed of 8000 r/min.

3. Experimental section

3.1. Film morphology

The film morphology and cross-section were characterized by SEM. Fig. 1a shows the original polymer film with some “dimples” on the surface, which is attributed to the “grafting to” mechanism. The “grafting to” mechanism exhibits the process that polymer chains form in solution and then graft onto the film [22–24]. The successively grafting of polymer chains causes the heterogeneity, but the cross-section image shows a dense polymer film without voids or other defects, indicating the “dimples” are very shallow (Fig. 1b). After 200 °C heating, as shown in Fig. 1c and d, these “dimples” disappear under the thermal motion of polymer chains and the film shows excellent microscopic homogeneity. The cross-section of the polymer film also exhibits well combined interface which should be attributed to the strong covalent bonding of the polymer film with Si surface. In addition, the thickness of the original polymer film is 157 nm (Fig. 1b), decreasing to 112 nm after 200 °C (Fig. 1d). The decrease of film thickness may be attributed to the chemical reaction and the shrink of polymer chains during heating process. Moreover, after 300 °C heating, the polymer film shows similar morphology with 200 °C heating, and the film thickness decreases to 88 nm (Fig. 1e and f). Thus, the heating process is effective for further improving the morphology of the grafted polymer film without destroying the chemical bond at the polymer/Si interface, but the film thickness will be affected.

In addition, the surface morphology and roughness were investigated by AFM. Fig. 2a shows the AFM image of the original polymer film, which exhibits the uniformly distributed “dimples” on the surface. However, these “dimples” are very shallow that the root mean square surface roughness is only 1.77 nm (Fig. 2b), which is consistent with SEM images. The smooth surface is attributed to the hydrophilic monomer and the surfactant (SDS). The hydrophilic monomer has high affinity to aqueous solution, and the surfactant can enhance the surface activity for grafting process. After 200 °C heating, the number of “dimples” reduces with the surface roughness decreases to 1.03 nm (Fig. 2c and d), which displays the thermal motion of the polymer chains. After 300 °C heating, the surface is very smooth that all dimples disappear with the roughness of only 0.46 nm (Fig. 2e and f). The height profiles of the polymer films are listed in Fig. S1, which shows the decrease of the height distribution after heating. Thus, heating process could help get smoother polymer film with extremely low surface roughness.

3.2. Structure transformation

The chemical structures of the polymer films were studied by XPS spectra, as shown in Fig. S2. The atomic concentration of C, N and O elements are listed in Table S1. Fig. 3 shows the high resolution C 1s and N 1s spectra of the polymer film. For the C 1s spectrum of the original polymer film, four main Gaussian peaks of C−C bond (284.76 eV), C−N and C−O bonds (285.74 eV), C═O bond (288.44 eV) and π–π^* shake up satellite (291.39 eV) are fitted, which confirms that the polymer film is composed of PMAA and nitrophenyl. N 1s spectrum exhibits three intense peaks at 405.65, 406.33 and 400.09 eV. The first two peaks are attributed to N−O bonds in $-NO_2$ groups and the last peak is assigned to N−H bond. Because N−H bond is reduced by $-NO_2$ groups (the only group containing N element in reagents), thus the products may be $-NH_2$ groups [25,26]. The generated $-NH_2$ groups with high activity makes it possible to form cross-linked amide rings. In addition, the division of $-NO_2$ peaks in nitrophenyl groups has been found, but the reason is not clear [27]. −NO and −NHOH groups are the production of incompletely reduced $-NH_2$ groups [28,29].

After 200 °C heating, C 1s spectrum shows four main peaks of C−C bond (284.66 eV), C−N and C−O bonds (285.60 eV), C═O bond (288.06 eV) and π–π^* shake up satellite (291.34 eV). N 1s spectrum