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Short communication

Annealing-free adhesive electroless deposition of a nickel/phosphorous layer on a silane-compound-modified Si wafer

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ABSTRACT

In this study, a post-annealing-free, adhesive nickel/phosphorous (Ni/P) layer was deposited on a 3-[2-(2-aminoethylamino)ethylamino] propyl-trimethoxysilane-modified (ETAS-modified) silicon (Si) surface through an electroless deposition process catalyzed by a novel polyvinylpyrrolidone-capped palladium nanocluster (PVP-nPd). ETAS was covalently bonded on the Si surface, whereas the amino groups on ETAS bridged with the palladium core in the PVP-nPd clusters. Because of the mentioned two effects, the deposited Ni/P layer showed superior adhesion on the Si wafer without the requirement of conventional annealing treatment. Compared with the Ni/P films deposited on bare and ETAS-modified Si surfaces by using commercial Sn/Pd colloids, the adhesion of the Ni/P film catalyzed by PVP-nPd on the ETAS-modified Si wafer improved 4- and 2-fold, respectively.

1. Introduction

Since its discovery more than 50 years ago [1,2], electroless deposition (ELD) of nickel/phosphorous (Ni/P) layers has been a valuable technique for creating diffusion barriers in the silicon (Si) industry, particularly in contact metallization, interconnecting different metals in integrated circuits, and fabricating microelectromechanical systems [3,4]. The ELD of Ni/P layers is a catalytic reaction that requires either a trace amount of seed Ni [5,6] or noble metals such as palladium [7,8] to lower the activation energy for nucleation and growth. Because the ELD process occurs on the catalyst-attached Si surface, the adhesion of Ni/P films is related to the interfacial properties of the catalyst and Si surface.

To enhance the bridging between the Si substrate and Pd catalyst, previous studies have developed a general approach for modifying Si surfaces with a self-assembling monolayer (SAM) created from an organosilane precursor [9,10]. After the dehydration of the organosilane-adsorbed Si, the hydrolyzable tail of the silane compound establishes a siloxane (Si – O – Si) covalent bond to the substrate; meanwhile, it also provides single or multiple head groups such as thiol or amine, which serves as a binding site for attaching catalysts. Studies involving this approach [11–13] have revealed that the SAM serves as an agglutinant for the substrate and catalyst. Compared with the silane compound and covalently bonded substrate, the silane compound and catalyst are weakly bonded. To obtain satisfactory interfacial strength between the ELD metal layer and substrate, a post-ELD annealing process is usually required to form intermetallic compounds. The objective of the current study was to develop a process for conducting ELD of a Ni/P film firmly adhered on texturized Si without performing a postannealing process.

2. Experimental

An N-doped P-type Si wafer (62.4 Ω/□) provided by Gintech Corporation was texturized in a 20% potassium hydroxide bath and cut into square pieces (2 cm × 2 cm). Next, the substrate was sequentially pretreated in a standard RCA process to remove organic species and 2% hydrogen fluoride (HF) solution to remove native SiO_2. To ensure the adsorption of the silane compound, the as-cleaned substrate was immersed into an ethanol solution containing 1% 3-[2-(2-Aminoethylamino)ethylamino]propyl-trimethoxysilane (ETAS, illustrated in Fig. 1a) for 30 min followed by sonication in pure ethanol for 10 min. Sonication was performed to remove aggregative ETAS that the substrate may have adsorbed. The ETAS modification was completed by baking the substrate at 120 °C for 30 min to form a Si – O – Si covalent bond on the Si surface.

A polyvinylpyrrolidone-capped palladium nanocluster (PVP-nPd) aqueous solution was synthesized according to the procedures provided in a previous study [14] and diluted to 50 ppm with deionized water, which is analogous to the concentration of Pd in commercial Sn/Pd colloidal solutions [15]. To adsorb catalysts for the ELD process, the ETAS-modified Si was immersed into the as-prepared PVP-nPd aqueous solution for 5 min at 40 °C without stirring. For comparison, a

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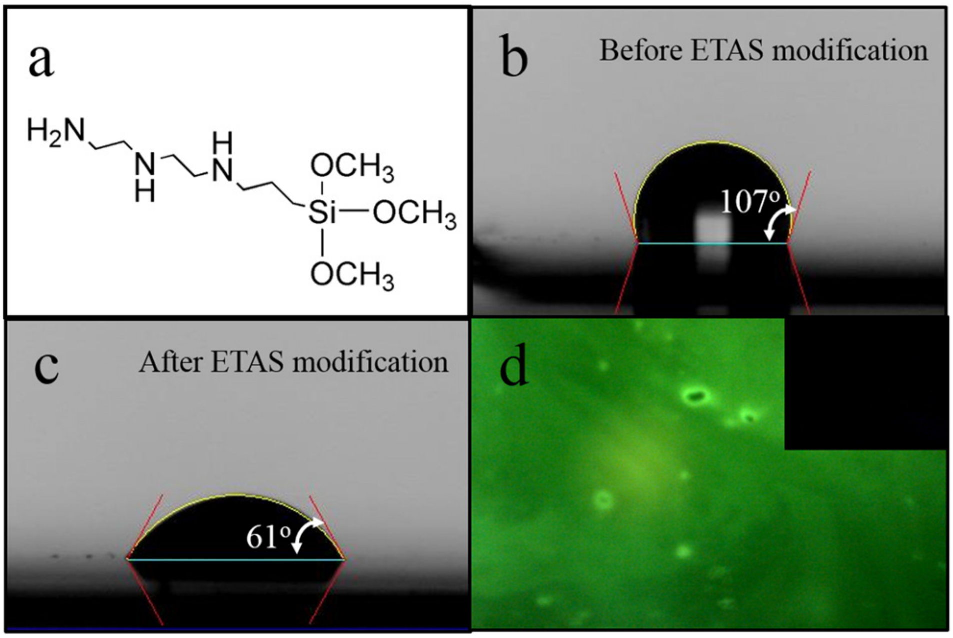

Fig. 1. (a) Molecular structure of ETAS, (b) water contact angle of the Si wafer before ETAS modification, (c) water contact angle of the Si wafer after ETAS modification, and (d) fluorecesnt labeling test on the ETAS-modified Si wafer; the upper right black image is the same as that for test on the unmodified wafer.

commercial Sn/Pd catalyst (9025M, OMG, USA) was also adsorbed on bare and ETAS-modified Si substrates.

The Ni/P film was deposited onto catalyst-attached Si substrates at 80 °C for 60 s in a commercial Ni/P bath (9026M, OMG, USA) by using the ELD process. After the Ni/P film deposition, a scanning electron microscope (SEM) was used to observe the film morphology. The Ni/P film was also cross-sectioned using the focused ion beam technique to observe the condition of the adhesion of this film on the Si substrate. The mechanical adhesion between the Ni/P ELD film and Si substrate was quantitatively measured using a pull-off adhesion tester (PosiTest AT-M, DeFelsko, USA) in accordance with ASTM D4541/D7234. The testing procedure involved sticking an aluminum dolly onto the film surface by using a thermally cured adhesive and then pulling off the dolly by applying a steadily increasing force, provided by the hydraulic pump, until the film detached from the surface. The highest pulling force representing the mechanical adhesion strength was recorded.

3. Results and discussion

The ETAS modification process was qualitatively examined according to the water contact angle and fluorescent labeling. Figs. 1b and c depict microscopic images of the water contact angle of the bare Si and ETAS-modified Si surfaces, respectively. The water contact angle decreased from 107° to 61° after ETAS was attached; the decrease in the water contact angle is attributable to the hydrophilic amino moieties on ETAS. Fig. 1d depicts fluorescent microscopic images of a fluorescein isothiocyanate (FITC)-labeled Si substrate at different stages of ETAS modification. As shown in the upper right corner of Fig. 1d, the bare substrate (after RCA cleaning and HF etching), as expected, had no fluorescent response; however, the main part of Fig. 1d indicates strong fluorescent illumination, and this is attributed to the interaction between FITC and amines [16,17], verifying the immobilization of ETAS on the substrate. The result also implies that the amino groups on ETAS are not involved in binding with Si. In a separate test, the fluorescent illumination remained unchanged even after 2 h of sonication, thus proving that ETAS covalently bonded to the Si surface.

Figs. 2a–c depict SEM images of the Ni/P ELD films deposited on the bare or ETAS-modified Si surface catalyzed by either Sn/Pd colloids or PVP-nPd. The coverage of the Ni/P film along the pyramidal Si was visually satisfactory, despite the difference in the surface conditions or catalysts. As depicted in Fig. 2c, two special finding can be observed: one is several particles were observed on the ELD film; these particles may have originated from the aggregation of the PVP-nPd nanoclusters. The other is ETAS residue was found in the bottom of valley between two pyramids; this residue may have resulted from insufficient sonication during the surface modification. These phenomena must be explored in detail in the future. In this study, the relationship between the film thickness and ELD time depicted in Fig. 2d shows that the universal ELD rate of was approximately 3 nm/s, indicating that neither ETAS modification nor the PVP-nPd catalyst changes the kinetics of ELD and, consequently, the possibility that different film structures formed during the following adhesion test can be excluded.

Fig. 3 illustrates the result of the pull-off test, indicating that the average adhesion strength of the ELD Ni/P film catalyzed by commercial Sn/Pd colloids on the bare (un-modified) Si substrate was 2.57 MPa in five samples and that the adhesion strength improved to 5. MPa when the Si surface was modified with ETAS. Regarding the PVP-nPd catalyst, the adhesion strength of the ELD Ni/P film on the ETAS-modified surface increased remarkably to 10.30 MPa, representing a 4-fold increase compared with that of the Ni/P film that was catalyzed by the commercial Sn/Pd catalyst on the unmodified surface. To efficiently prove the advantage of the ETAS and PVP-nPd combination, a postannealing process (at 400 °C for 30 s) was applied on the sample of the unmodified Sn/Pd-catalyzed Ni/P film. The results indicated that the adhesion strength, as expected, increased to 6.01 MPa; although this improvement is substantial, it is still lower than that of the ETAS-modified, PVP-nPd-catalyzed Ni/P film.

In this study, various Si samples were examined using X-ray photoelectron spectroscopy (XPS) to explain this substantial improvement. The plots illustrated in Fig. 4, from the bottom to the top, show the N1s XPS spectra of the ETAS-modified (ETAS), ETAS-modified with Sn/Pd adsorbed (ETAS + Sn/Pd), ETAS-modified with PVP-nPd adsorbed (ETAS + PVP-nPd), and only PVP-nPd-dipped (PVP-nPd) Si wafers, respectively. The N1s signal of ETAS demonstrated a main peak of free amine (NH_2 at 398.1 eV, dashed green line) and a shoulder of a hydrogen-bonded amino group (NH_3^+ at 399.4 eV, dashed red line),