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Modification of the Mechanical Properties of SiO_2 Thin Film Using Plasma Treatments for Micro-Electro-Mechanical Systems Applications

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In this study, we developed a novel method of modifying thin-film mechanical properties by plasma surface modification. In order to demonstrate the feasibility of this approach, various plasma treatments, including exposure to O_2, H_2, and NH_3 atmospheres, were implemented to modify the mechanical properties, including Young's modulus, residual stress, and hardness, of SiO_2 films. The experimental results show that the mechanical properties have been changed following the formation of Si–N and Si–H bonds. These characteristics can be employed to change the shape and resonant frequencies of micromachined beams for micro-electro-mechanical systems (MEMS) applications. Since plasma treatment is simple and easy to integrate with existing processes, it has the potential to be an efficient way to finely modify the mechanical characteristics of MEMS structures. [DOI: 10.1143/JJAP.47.5242]

KEYWORDS: plasma treatment technology, micro-electro-mechanical systems (MEMS), mechanical properties, chemical properties, microcantilever

1. Introduction

Thin films from semiconductor processes are of special interest to academics and industries involved in fabrication of microelectronic devices and micro-electro-mechanical systems (MEMS). For example, the mechanical properties of thin films, such as Young's modulus and residual stress, are very critical to the performance of MEMS devices. In general, thin films have different mechanical properties from their bulk counterparts. The mechanical properties of thin films may even vary with the fabrication process as well as film thickness. Recently, various approaches to modify the mechanical properties of thin films during fabrication processes have been presented.[1,2] Changing the deposition (or growing) conditions is the most straightforward approach to tune thin-film mechanical properties. For example, the residual stress of a sputtered film can be altered from tension to compression by varying film thickness.[3] Another possible approach is to reduce net residual stresses by depositing a compensatory film.[4]

Plasma treatment has various applications to thin films, for example, thin-film surface cleaning,[5] modification,[6] adhesion,[7] electrical,[8] optical,[9] and corrosion properties.[10] Plasma treatment can change the surface characteristics of films while retaining their inherent properties.[11] For instance, the effects of various gas plasma treatments on SiO_2 aerogel films have been investigated,[12] so as to control the surface chemical species and improve electric properties. Most plasma cleaning operations can render the surface more wettable (hydrophilic) than in the case of without plasma treatment. It is also possible to fabricate nonwettable (hydrophobic) surfaces with the proper choice of gas and treatment conditions. Plasma treatment leads to the cleaning of the surface by ionic bombardment, surface oxidation, cross linkage, and surface grafting/chemical reaction.[13] Plasma treatment is a very general process in IC industry. From surface cleaning to surface modification, it is constantly the process of choice. Moreover, it can be applied using many types of equipment used in semiconductors, such as those in plasma-enhanced chemical vapor deposition (PECVD) and reactive ion etching (RIE).

In this study, plasma treatment has been employed to change the mechanical properties of thin SiO_2 films. The variation of SiO_2 films mechanical properties after treatment with different plasmas is investigated by two approaches. The first approach is to measure the tip deflection of a suspended microcantilever made of a treated film. The second approach is to characterize the equivalent Young's modulus, hardness, surface bonding, and depth profile of the film before bulk silicon etching.

2. Experimental Procedure

Plasma-treated thermal SiO_2 films have been employed to demonstrate the feasibility of the present study. Various plasma treatments, including O_2, H_2, and NH_3 plasmas, of the SiO_2 surface have been investigated. Moreover, the treatments of SiO_2 films using the combination of two NH_3 plasmas under different conditions have also been studied. A SiO_2 film and a freely suspended SiO_2 thin structure are characterized to evaluate the performance of plasma treatments.

2.1 Sample preparation

The test SiO_2 film and cantilever were prepared using a standard bulk micromachining process, as schematically shown in Fig. 1. The 1- and 0.8-μm-thick SiO_2 films were thermally grown at 1050 °C on a 4-in. bare silicon wafer. The SiO_2 thin films were patterned by photolithography and RIE, as shown in Fig. 1(a). An aluminum film was deposited and patterned using the lift-off process. This aluminum film acted as the mask to define the region for the subsequent plasma treatment. After that, various plasmas were employed to modify the surface property of the SiO_2 film, as shown in Fig. 1(b1). The plasma treatment time was 1 h. The plasma treatments were operated in a PECVD reaction chamber. The conditions of plasma treatments are listed in Tables I and II. As illustrated in Fig. 1(c1), the aluminum film was etched away using an etching solution (H_3PO_4:HNO_3:CH_3COOH:H_2O) at 75 °C. Finally, the silicon substrate was removed anisotropically using 15%

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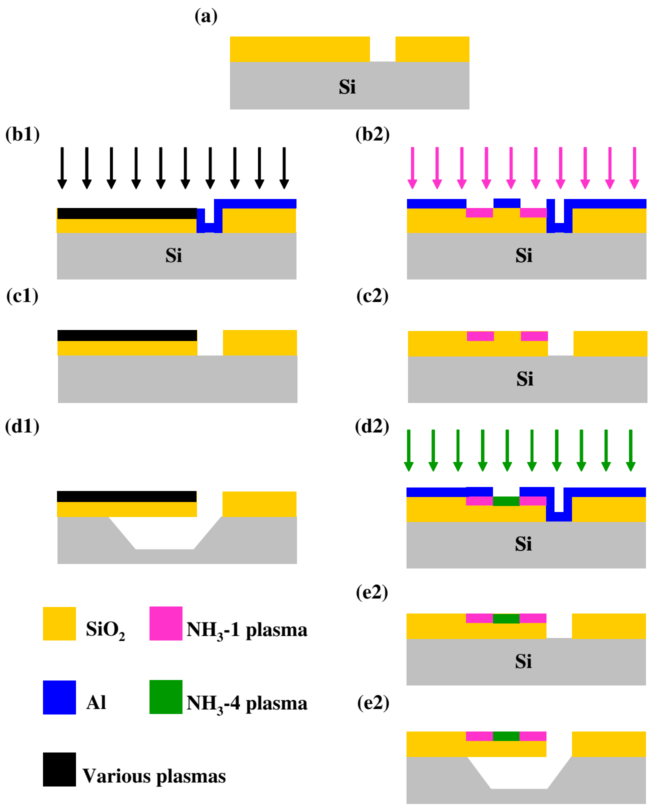

Fig. 1. (Color online) Flow chart for various plasma treatments of cantilever beam.

Table I. Experimented parameters and conditions for plasma treatments.

Plasma	Flow rate (sccm)	Pressure (mTorr)	Temp. (°C)	Power (W)
NH_3	700	300	250	200
O_2	900	600	100	300
H_2	800	800	100	100

Table II. Experimented parameters and conditions for NH_3 plasma treatments.

Exp. no.	Flow rate (sccm)	Pressure (mTorr)	Temp. (°C)	Power (W)
NH_3-1	600	300	100	200
NH_3-2	700	500	100	200
NH_3-3	700	300	250	200
NH_3-4	600	500	250	200

tetramethylammonium hydroxide (TMAH) solution at 75 °C, so that the cantilevers made of the 1-μm-thick SiO_2 film were completely suspended, as shown in Fig. 1(d1). In this case, the lengths of SiO_2 cantilevers ranged from 5 to 300 μm.

In this study, we also established another process to treat SiO_2 films by the combination of two NH_3 plasmas under different conditions, as shown in Figs. 1(b2)–1(e2). As shown in Fig. 1(b2), the aluminum film also acted as the mask to define the region for the subsequent NH_3-1 plasma treatment. Figure 1(c2) shows the pattern formed by the NH_3-1-plasma-treated SiO_2 film after removing the aluminum mask. In this case, the SiO_2 cantilevers were treated using the NH_3-1 plasma only at some regions. Following the same processes as those shown in Figs. 1(b2)–1(c2), a NH_3-4-plasma-treated region was also defined, as illustrated in Figs. 1(d2)–1(e2). The conditions of NH_3-1 and NH_3-4 plasma treatments are listed in Table II. The silicon substrate was also removed anisotropically using 15% TMAH solution at 75 °C, so that the cantilevers made of the 0.8-μm-thick SiO_2 film was completely suspended, as shown in Fig. 1(e2). The length and width of this SiO_2 cantilever were 300 and 28 μm, respectively.

2.2 *Characterization*

A nano-indentation test, X-ray photoelectron spectroscopy (XPS), and secondary ion mass spectrometry (SIMS) were employed to characterize the films before bulk silicon etching. The hardness of the films was characterized using a Berkovich indenter during the indentation test.[14)] The chemical properties of the thin films, such as chemical composition, were investigated by XPS and SIMS. XPS spectra were recorded on a PHI1600 ESCA system made in the United States (test conditions: Mg Kα (1253.6 eV); power, 250 W). The N 1s, O 1s, and Si 2p photoelectron peaks were recorded. The step size was 0.1 eV and the dwell time was 1000 ms. In this study, the analysis of XPS spectra involved background subtraction using the Shirley method,[15)] and then the nonlinear least squares fitting to the mixed Gaussian–Lorentzian peak shape was carried out. The variation of the chemical properties with the depth of thin films was also characterized.

Nondestructive tests, including the static load-deflection bending test and dynamic resonant test, were employed in this study to characterize the mechanical behaviors of the cantilevers. The static deformation of the cantilevers was examined to determine the equivalent gradient residual stresses of the SiO_2 films.[3)] The deflection profile of the SiO_2 cantilever was measured using an optical interferometer. Moreover, the resonant frequency of the cantilever was employed to determine the equivalent Young's modulus of the SiO_2 film.[16)] During the vibration test, the bulk lead zirconium titanate (PZT) was employed as a shaker to excite the micromachined cantilevers. The dynamic response of the cantilevers was measured using a laser Doppler vibrometer (LDV) and recorded using an oscilloscope and a dynamic signal analyzer. In order to eliminate the effect of air damping, the dynamic test was conducted inside a vacuum chamber. The ambient pressure inside the chamber can be reduced to 1 mTorr. Thus, the variations of equivalent gradient residual stresses and equivalent Young's modulus with different plasma treatments were determined.

3. Results and Discussion

As shown in Fig. 1, the samples were prepared using two different approaches. The following experimental results obtained from the samples treated by the processes shown in Figs. 1(b1)–1(d1) and Figs. 1(b2)–1(e2). To evaluate the mechanical properties of the thin films after plasma treatments, the tip deflection of a suspended microcantilever made of the treated film was measured. In addition, the equivalent Young's modulus, hardness, surface bonding, and depth profile of the film were also characterized.

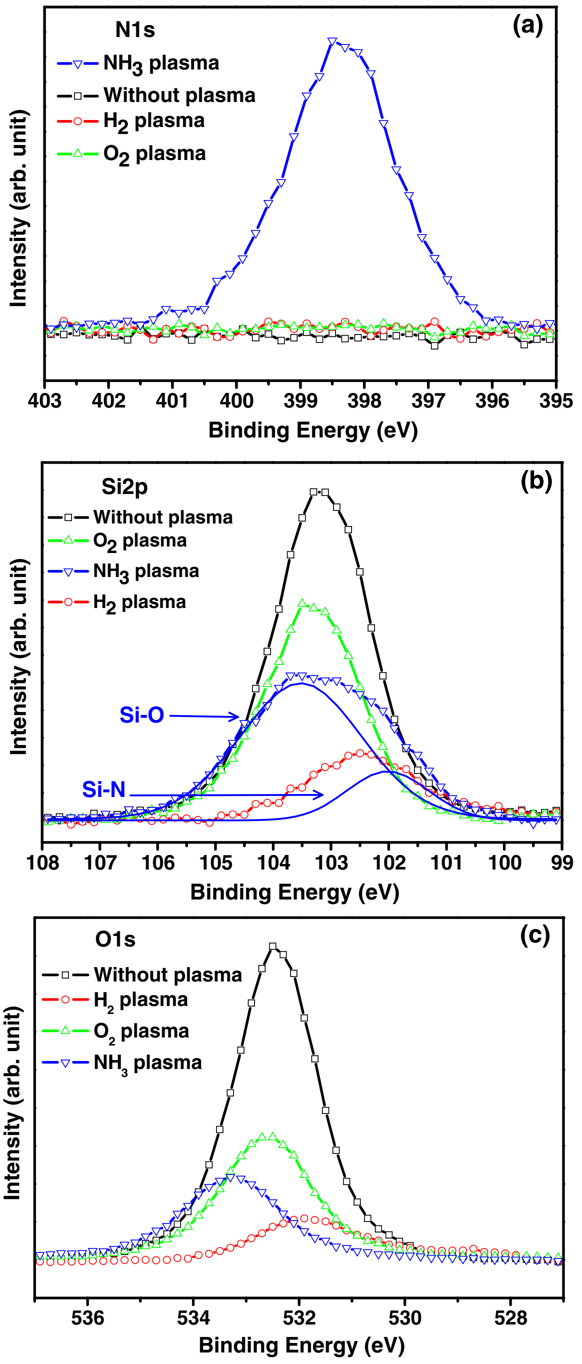

Fig. 2. (Color online) XPS spectra of SiO_2 film at (a) N 1s, (b) Si 2p, and (c) O 1s lines for various plasma treatments.

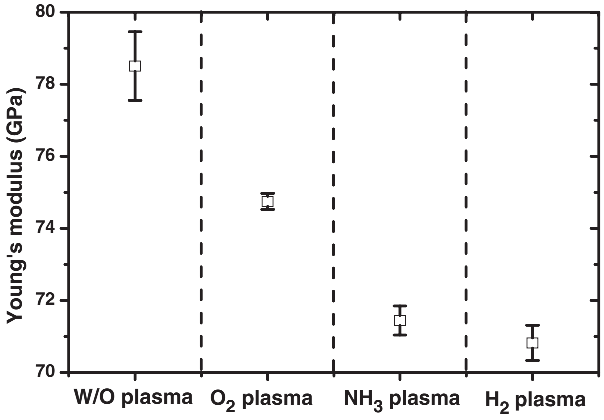

Fig. 3. Equivalent Young's modulus of SiO_2 with various plasma-treated surfaces determined from the dynamic response of the cantilevers.

3.1 Treatment with single plasma

In this section, we report on the variation of thin-film mechanical properties after the treatments with O_2, H_2, and NH_3 plasmas. These gases have different chemical reactivities and atomic masses, and may exert different effects on the mechanical properties of thin SiO_2 films. The chemical bonding of thin films after plasma treatment was characterized by XPS. Thus, the correlation between mechanical properties and chemical bonding of thin films was obtained. Figures 2(a)–2(c) shows the XPS spectra of the SiO_2 film for N 1s, Si 2p, and O 1s lines after various plasma treatments, respectively. The peak in Fig. 2(a) indicates that the Si–N bond was formed after NH_3 plasma treatment.[17] As shown in Fig. 2(b), the binding energies of the Si 2p electrons for samples with or without O_2 plasma treatment were all near 103.2 eV.[18] In addition, the binding energy of the sample after H_2 plasma treatment was slightly decreased to about 102.5 eV. It implies that some of the Si–O bonds were replaced by the Si–H bonds,[19,20] so that part of the oxidation state of silicon was less than four. Similarly, the SiO_2 film treated with NH_3 plasma was composed of two different environments in the Si 2p line: Si–O at 103.6 eV and Si–N at 102.1 eV.[17,18,21] In addition, the binding energy of the sample after NH_3 plasma treatment slightly changed. It implies that some of the Si–O bonds were replaced by the Si–N bonds, so that part of the oxidation state of silicon was less than four. As shown in Fig. 2(c), the binding energies of the O 1s electrons for the samples with O_2 plasma treatment or without any plasma treatment were all near 532.5 eV.[18] In addition, the binding energy of the O 1s electrons decreased after the H_2 plasma treatment, since part of the Si–O p–d π back bonds were replaced by the Si–H bonds.[22] On the other hand, the binding energy of the sample increased after the NH_3 plasma treatment, because the Si–N bonds enhanced the Si–O back bonds owing to the high electronegativity of nitrogen.[22]

The equivalent Young's modulus of SiO_2 film measured using the resonant beam approach after various plasma treatments are shown in Fig. 3. The equivalent Young's modulus of the SiO_2 film without plasma treatment was 78.5 GPa. The equivalent Young's modulus of the films after treatment with H_2, O_2, and NH_3 plasmas were 70.8, 74.8, and 71.5 GPa, respectively. Hence, the equivalent elastic modulus of the SiO_2 films changed by about 10% following the H_2 as well as NH_3 plasma treatment.

The peak of the equivalent gradient residual stress σ_1 can be determined by measuring the radius of the curvature (ρ) of a bent cantilever.

$$\sigma_1 = Eh/2\rho \tag{1}$$

Here, E and h are the elastic modulus and thickness of the SiO_2 film, respectively. The deflection profiles of the cantilever were measured using the optical interferometer. The measured deflection profiles of cantilevers (and their SEM images) subjected to various plasma treatments are shown in Fig. 4. The radius of the curvature of a 200-µm-long cantilever was 1.85 mm before plasma treatment, and

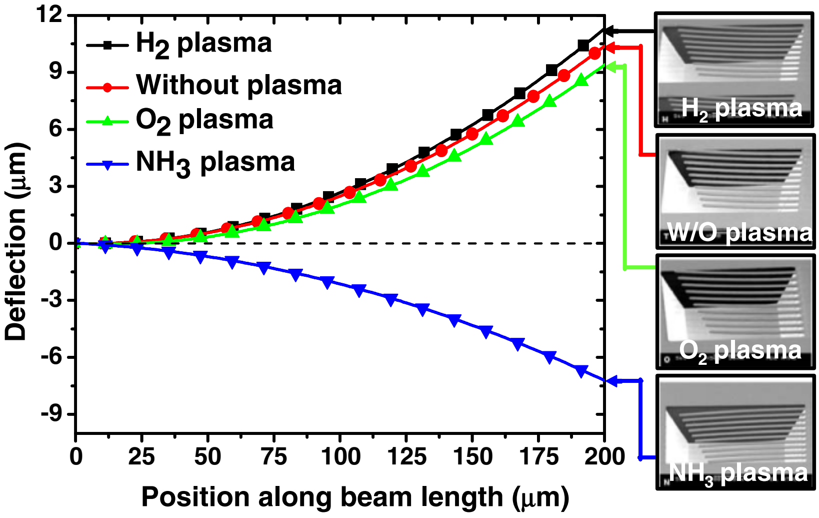

Fig. 4. (Color online) Measured deformation profiles of cantilever beams with various plasma-treated surfaces.

the equivalent gradient residual stress was 21.01 MPa. After treatment with H_2, O_2, and NH_3 plasmas, the radius of the curvature of the 200-μm-long cantilever became 1.67, 1.86, and −3.40 mm, respectively; thus, the equivalent gradient residual stresses σ_1 became 20.59, 20.04, and −10.65 MPa, respectively. Therefore, the mechanical property of the film after NH_3 plasma treatment was significantly changed.

In general, the thin-film equivalent gradient residual stresses can be modified by physical and chemical methods of plasma treatment.[23–25] For instance, ion bombardment is a well known physical effect,[23] whereas the formation of chemical bonds is a typical chemical approach.[24,25] In this study, the O_2 plasma treatment leads to a compressive residual stress on the surface, so that the equivalent gradient residual stress bent the cantilever concave downward. This compressive residual stress was predominated by ion bombardment (physical effect).[23] On the other hand, the H_2 plasma treatment leads to a tensile residual stress on the film surface, so that the equivalent gradient residual stress bent the cantilever concave upward. This tensile residual stress may result from the formation of Si–H bonds (chemical effect), as shown in Figs. 2(b) and 2(c). The NH_3 plasma treatment leads to a compressive residual stress on the surface, so that the equivalent gradient residual stress bent the cantilever concave downward. This compressive residual stress may result from the formation of Si–N bonds (chemical effect), as shown in Fig. 2(a). Figure 5 shows the variation of the beam curvature with time for different plasma treatments. The variation of the beam curvature is smaller than 1% for 30 months without controlling the humidity and temperature of the environment.

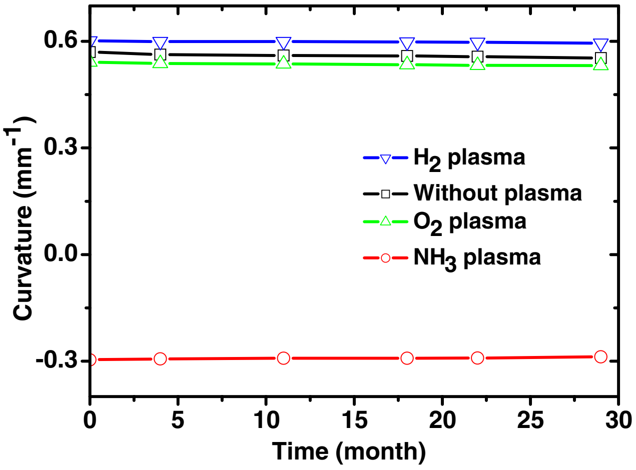

Fig. 5. (Color online) Deviation of stress beam deflection during 30 months.

Table III. Control factors and their levels.

	Control parameter (Factor)	Operating condition (Level)	
A	Temperature (°C)	100	250
B	Pruessure (mTorr)	300	500
C	Flow rate (sccm)	600	700

3.2 *Combination of two NH_3 plasma treatments*

As shown by the study described in §3.1, the NH_3 plasma treatment has a significant effect on the SiO_2 film. Thus, this section, we further discuss the effect of the mechanical properties on the thin SiO_2 film induced by the combination of two different NH_3 plasma treatments. The SiO_2 thin film was exposed to different NH_3 plasma treatment conditions using the Taguchi method.[26] The three control parameters (designated as factors in the Taguchi method) and their related operating conditions (designated as levels in the Taguchi method) of these NH_3 plasma treatments are listed in Table III. These three parameters include substrate temperature, chamber pressure, and NH_3 gas flow rate. According to the Taguchi method, in this study, we conducted four experiments (designated as NH_3-1, NH_3-2, NH_3-3, and NH_3-4) on the basis of the conditions shown in Table II.

As shown in Fig. 6, the SIMS depth profile of the NH_3-plasma-treated SiO_2 film was investigated. The plasma conditions are listed in Table II. Thus, the variation of the chemical composition with the depth of the SiO_2 film was determined. Figure 6 shows the depths of the SiO_2 film as

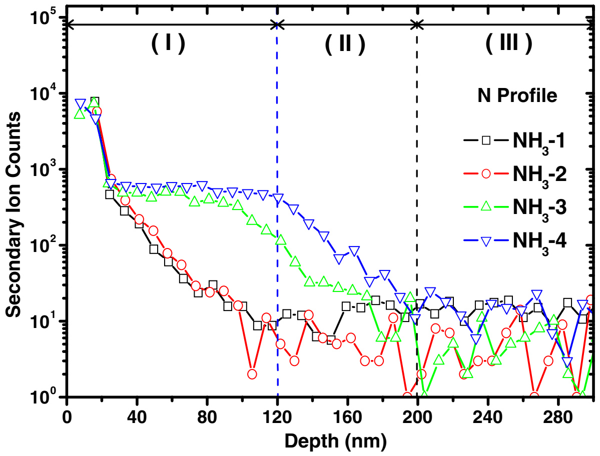

Fig. 6. (Color online) SIMS depth profiles of SiO_2 films with various plasma treatments.

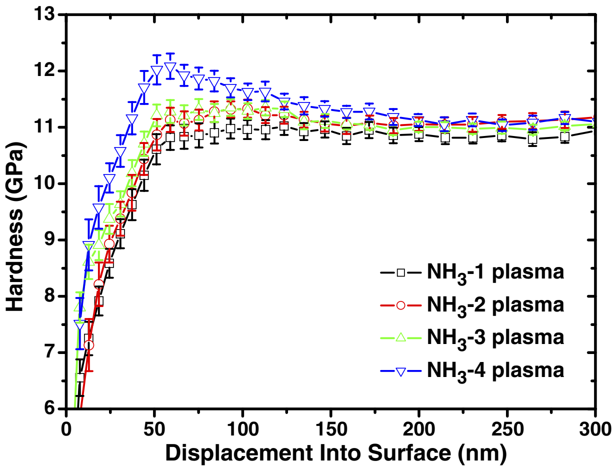

Fig. 7. (Color online) Hardness as a function of displacement into surface for SiO_2 with various NH_3 plasma condition treated surfaces.

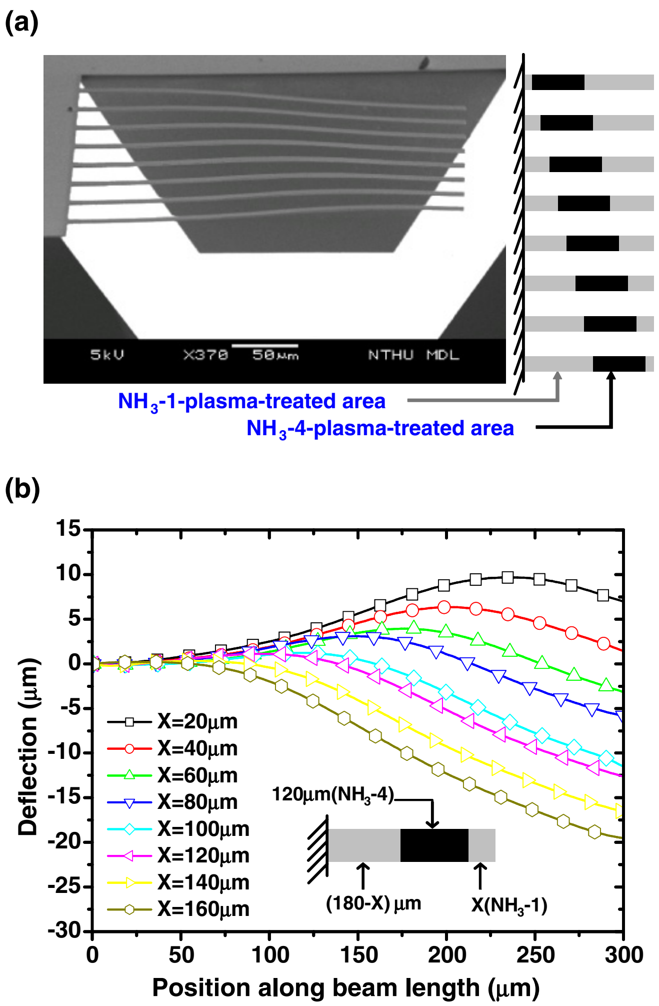

Fig. 8. (Color online) (a) SEM images of cantilever beams for two different plasma treatments at various regions, and (b) deflection of cantilever beams for two different plasma treatments at various regions.

three regions with different nitrogen profiles. The numbers I, II, and III indicate the regions of higher nitrogen profile, lower nitrogen profile, and no nitrogen, respectively. The nitrogen implantation depths for NH_3-1, NH_3-2, NH_3-3, and NH_3-4 plasma treatments are 120, 120, 180, and 200 nm, respectively. In region III (from 200 to 300 nm in depth), the nitrogen profile of the SiO_2 film was not affected by the plasma treatments. In addition, the SiO_2 film treated with NH_3-3 and NH_3-4 plasma at a higher substrate temperature and a higher NH_3 concentration had a higher nitrogen profile and a deeper nitrogen penetration. The formation of Si–N chemical bonds on the surface (120 to 200 nm in depth) of the SiO_2 film will lead to an equivalent gradient residual stress; moreover, this gradient residual stress can easily be changed by varying the conditions of NH_3 plasma.

Figure 7 shows that the depth profiles of hardness of the SiO_2 film vary with the conditions of NH_3 plasma treatment. The results are the average of nine indentations with the error bars representing the standard deviation. The hardness for the four different NH_3 plasma treatments (NH_3-1, NH_3-2, NH_3-3, and NH_3-4) at 60 nm had maximum values of 10.81, 11.13, 11.28, and 12.08 GPa, respectively. It shows that film hardness is affected by nitrogen penetration depth, and reaches the maximum after treatment with NH_3-4 plasma. In general, film hardness ranges from 9.4 to 22.1% for these NH_3 plasma treatments.

NH_3 plasma treatment can be exploited to change the shape of the micromachined cantilever. A SEM image in Fig. 8(a) shows the deflection profiles of SiO_2 cantilever beam after treatment with NH_3-1 and NH_3-4 plasmas along beam length. These cantilevers were fabricated using the processes shown in Figs. 1(b2)–1(e2). The difference in the deflection profiles of the cantilevers is even visible in the SEM image. The plasma-treated regions are indicated on the right hand side of Fig. 8(a). Gray indicates the area treated with NH_3-1 plasma, and black indicates the area treated with NH_3-4 plasma. The deflection profiles of the cantilever measured using the optical interferometer are shown in Fig. 8(b). The symbols "X" and "180-X" indicate the regions treated with NH_3-1, and the NH_3-4-plasma-treated region remained at 120 µm. The measured deflection profiles consist of concave upward and concave downward segments when the cantilever was treated with NH_3-1 and NH_3-4 plasmas. Briefly, the concave upward segment is associated with the NH_3-1 treatment, and the concave downward segment is associated with the NH_3-4 treatment. The experimental results demonstrate that the shape of the cantilever can be modified using the combination of plasma treatments along beam length. A flat cantilever can be achieved if the equivalent stress gradient resulting from the plasma treatment is equal and opposite to the residual stress gradient of the SiO_2 film. Moreover, using the combination of plasma treatments along beam width can also generate a flat cantilever.[24]

4. Conclusions

In this study, we developed a novel method of modifying thin-film mechanical properties by plasma surface modification. In order to demonstrate the feasibility of this approach, various plasma treatments, including exposures to O_2, H_2, and NH_3 atmospheres, were implemented to modify the hardness, equivalent Young's modulus, and equivalent gradient residual stress of SiO_2 films. The formation of Si–N chemical bonds on the surface (120 to 200 nm in depth) of SiO_2 films will lead to an equivalent gradient residual stress; moreover, this gradient residual stress can easily be changed by varying the conditions of NH_3 plasma. These characteristics can be employed to modify the shape of the micromachined beams for MEMS applications. The variation of beam curvature is smaller than 1% for 30 months without controlling the humidity and temperature of the environment. In addition, the equivalent Young's modulus of SiO_2 films can be modified by plasma treatment; and, the resonant frequencies of the micromachined beams can also be changed. This characteristic has extensive applications in MEMS resonant components. Since plasma treatment is simple and easy to integrate with existing processes, it has the potential to be an efficient way to finely modify the mechanical characteristics of MEMS structures.

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