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Surface wettabiliy of nitrogen plasma-implanted silicon

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Abstract

Silicon wafers were implanted with nitrogen by plasma immersion ion implantation (PIII) to alter the surface hydrophilic properties and wettability. Our X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and contact angle measurements indicate that the Si–N bonds formed during the plasma implantation process are the main reason for the enhancement of wettability. The phenomenon can be explained in terms of the surface energy determined from our contact angle measurements. Owing to the non-UHV (ultrahigh vacuum) conditions inherent to most PIII instruments, there is competition between the formation of surface Si–O and Si–N bonds and the nitrogen retained dose is crucial to the final wettability of the plasma treated silicon wafers.
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1. Introduction

Silicon nitride intrigues scientists and technicians due to its attractive physicochemical as well as mechanical properties and the materials are used in various applications including microelectronics, optoelectronics, solar cells, protective coatings against wear and corrosion and so on. However, silicon nitride has been relatively unexplored as a biomaterial until recently. It may be because researchers have focused on the dielectric, optical and mechanical properties of the materials instead of its potentially remarkable physicochemical characteristics in biomedical applications, although other silicon based materials such as silicone rubber, SiO_2 and SiC have been investigated for this purpose and been shown theoretically and experimentally to offer good biocompatibility. In the work described in this paper, we employed plasma immersion ion implantation (PIII) to introduce nitrogen into silicon wafers and evaluated one of the most important surface properties, wettability, from the perspective of biomedical applications. Wettability is often referred as hydrophilicity and considered to be a very important surface property of materials and particularly crucial to interfacial reactions occurring between the biomaterials interface and biological tissues [1]. Our results show that nitrogen PIII can indeed improve the surface wettability of silicon and is thus a potential versatile surface modification in biomedical engineering [2].

2. Experimental details

Silicon (100) wafers were processed in our PIII instrument [3–5] with a base pressure of 8×10^{-6} Torr. The samples were first sputter cleaned for 10 min using 500 W radio-frequency (RF) argon plasma. Nitrogen was then bled into the instrument to a partial pressure of about 5.5×10^{-4} Torr and the plasma was ignited by 1000 W RF. Plasma implantation was conducted by applying a pulsed voltage to the samples. The implant dose and depth were tailored by adjusting the negative sample bias, and in

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Table 1
PIII parameters

Sample	Target bias voltage			RF power (W)	Working pressure (10^{-3} Torr)	Time (min)
	Voltage (kV)	Frequency (Hz)	Pulse width (μs)			
#1	30	200	30			
#2	30	300	30			
#3			50	1000	5.3	120
#4			80			
Si–O (Ctr.)	30	200	100			

our experiments, four different pulse widths were used to achieve different nitrogen retained doses. Silicon oxide films as control samples were prepared using a similar process but in oxygen plasma. The operating parameters are summarized in Table 1.

Fourier transform infrared spectroscopy (FTIR) was conducted using a Perkin–Elmer 1600 to determine the bonding states in the films. The absorbances were measured between 400 and 2000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5600 equipped with a monochromatic AlK_α X-ray source to determine the composition and chemical states of the film. The XPS spectra were acquired after sputter cleaning for 2 min by argon.

The surface wettability was evaluated by the sessile drop method employing a JY-82 contact angle goniometer. Doubly distilled water and five additional test liquids (glycerin, formamide, diiodomethane, glycol and tritolyl phosphate) were used to determine the wettability as well as surface energy of the samples using archival relative surface tension components of the test liquids [6]. In each individual test, six measurements were conducted to obtain good statistics and the surface energy of the films was calculated using the Zimans and Good method [6].

3. Results and discussion

Fig. 1 presents the XPS surface spectra of the four samples, and Table 2 lists the surface compositions determined from the spectra. Our calculations show that the nitrogen implant dose does not increase linearly with larger voltage pulse widths. Samples #2 and #3 have the highest retained dose while sample #1 possesses a lower nitrogen dose due to a shorter implantation time and sample #4 shows the lowest dose in spite of the longest voltage pulse. The anomaly has also been observed by Ueda et al. [7] who suggested that it was caused by strong etching of the Si surface by the nitrogen plasma under high voltage. A significant amount of surface oxygen is also detected arising from the nature oxide that has not been totally removed before our analysis and more likely our non-UHV (ultrahigh vacuum) conditions of our PIII chamber. Co-implantation of oxygen is in fact quite common in PIII experiments.

Fig. 2 shows the FTIR absorbance spectra of the synthesized films showing the formation of Si–N. A strong

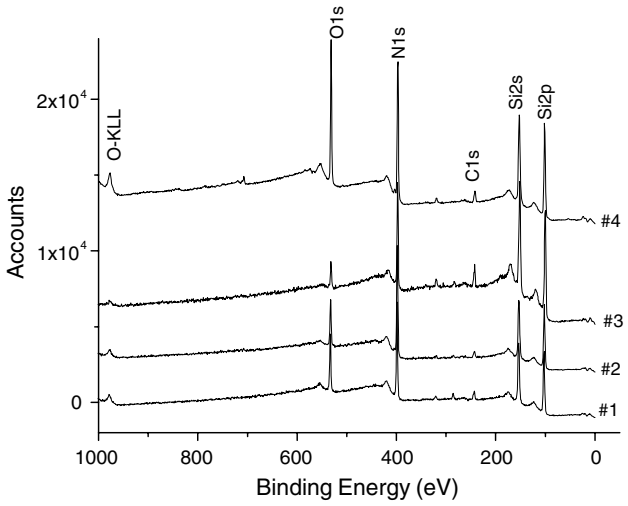

Fig. 1. XPS spectra acquired from the four samples shown in Table 1.

Table 2
Compositions of the nitrogen plasma-implanted silicon wafers as determined by XPS

Samples	Elements			
	C (C1s)	O (O1s)	N (N1s)	Si (Si2p)
#1	0.28	26.79	28.91	44.02
#2	0.87	15.36	39.18	44.6
#3	0.04	20.17	34.67	44.62
#4	0.02	29.61	26.32	44.05

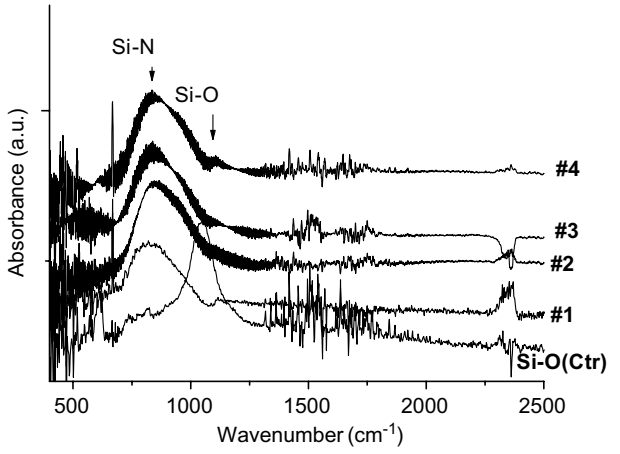

Fig. 2. FTIR absorbance spectra of the samples.

absorption band centered at approximately 830–865 cm^{-1} corresponding to the asymmetric in-plane Si–N stretching vibration mode [8,9] can be observed in all the samples. Our results also show increasing peak intensity with higher N implant dose. The small peaks at around 500 cm^{-1} are attributed to the Si–N vibrational mode [8]. The SiO_2 control sample shows one strong peak at around 1050 cm^{-1} and this peak appears as a weak form in the spectra acquired from samples #1 and #4.

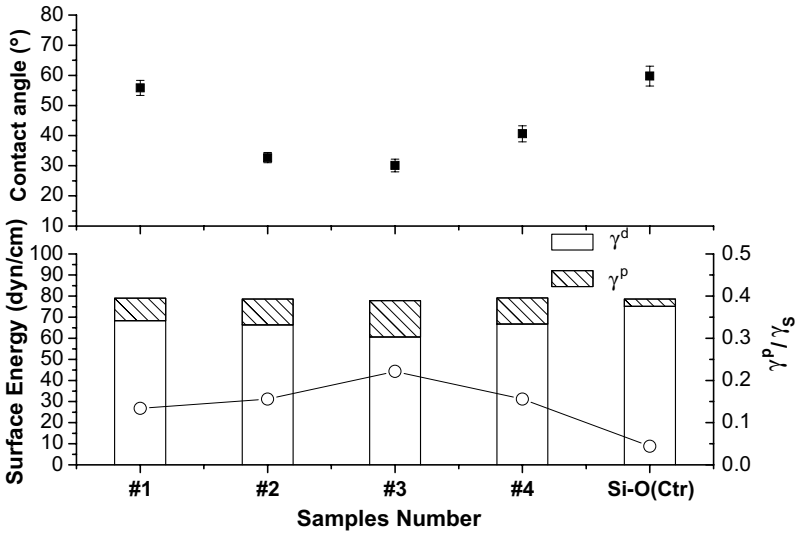

Fig. 3. Water contact angles, surface energy and polar contribution ratio of the samples determined from the contact angle test results.

The water contact angle is an indication of the surface hydrophilic property of the films and depends largely on two factors, dispersion γ^d and polar γ^p, that dictate the surface energy. The dispersion contribution is built up from a single interaction, which is generated by the movement of electrons around an atom or molecule, while the latter is established from different forces/interactions like hydrogen bonds, covalent bonds and dipole–dipole interactions. The larger the polar contribution to the surface energy, the higher is the tendency of the surface to attract polar liquids and the higher the water wettability. The surface energy, defined as the sum of the dispersion and polar contribution, can be determined by contact angle measurements and calculated by solving Young's equations using more than three testing liquids/solid interfaces combined with the work of adhesion [6,10]. Fig. 3 shows water contact angles measured by the sessile drop method and the surface energy calculated by the Zimans method. Samples #3 and #2 are very hydrophilic exhibiting small water contact angles of 30.8° and 32.7°, respectively, whereas samples #1 and #4 show contact angles of 55.8° and 41.2°, respectively and are thus less hydrophilic. In comparison, the SiO_2 control sample has the highest contact angle of 59.8°. The surface energy γ_s consists of two components: γ^d and γ^p. Commonly, the higher the surface energy of the solid substrate relative to the surface tension of the liquids, the better is the wettability and the smaller the contact angle. However, the difference in the polar contribution to the total surface energy plays a critical role in determining the wettability for a polar liquid like water [10]. In our study, all the samples show similar surface energy but different water wettability due to the large difference in the polar component ratio (γ^p/γ_s) as described in Fig. 3. Samples #2 and #3 thus possess high wettability on account of the high polar contributions from the higher nitrogen implant dose and more abundant Si–N bonds. In our experiments, a smaller nitrogen dose implies a higher oxygen dose translating into more Si–O bonds which are more hydrophobic. Our results thus indicate that the nitrogen retained dose plays an important role in the wettability of plasma implanted silicon.

4. Conclusion

The surface hydrophilic properties of nitrogen plasma-implanted silicon vary with the relative amount of the Si–N bonds. The nitrogen retained dose depends on many processing conditions such as exposure time to the plasma, bias voltage and voltage pulse width. Our results indicate that Si–N bonds enhance the wettability by providing a higher polar contribution to the surface energy of the film. Owing to the non-UHV conditions in most PIII instruments, there is a competition between the formation of surface Si–O and Si–N bonds. These two types of bonds affect the wettability in an opposite manner and so tight control of these bonds is important in achieving the desired property. More work is being conducted in our laboratory to increase the nitrogen retained doses while reducing the formation of competing Si–O bonds on the surface.

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