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MeV-ion beam analysis of the interface between filtered cathodic arc-deposited *a*-carbon and single crystalline silicon

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Abstract

Amorphous carbon (*a*-C) films were deposited on Si(100) wafers by a filtered cathodic vacuum arc (FCVA) plasma source. A negative electrical bias was applied to the silicon substrate in order to control the incident energy of carbon ions. Effects of the electrical bias on the *a*-C/Si interface characteristics were investigated by using standard Rutherford backscattering spectrometry (RBS) in the channeling mode with 2.1-MeV He^{2+} ions. The shape of the Si surface peaks of the RBS/channeling spectra reflects the degree of interface disorder due to atomic displacement from the bulk position of the Si crystal. Details of the analysis method developed are described. It was found that the width of the *a*-C/Si interface increases linearly with the substrate bias voltage but not the thickness of the *a*-C film.

Key words: Rutherford backscattering spectrometry (RBS), Channeling, Amorphous carbon, Interface, Filtered cathodic vacuum arc (FCVA)

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1 Introduction

Amorphous carbon (a-C) has been of great interest for its outstanding mechanical and electrical properties, such as wide band gap, high hardness, wear resistance and optical transparency [1,2]. These unique properties have been fascinated for numerous applications. In general, the a-C films exhibit a variety of structural features and properties that depend on the fraction of sp^3 and sp^2 bonding in the films. It is well known that a-C films deposited by cathodic arc plasma have large compressive stress correlated with a higher fraction of the sp^3 bonding, which leads to poorer adhesion, especially when a thicker film is required. The fraction of the sp^3 bonding depends on the incident energy of carbon ions that strike on growing carbon films [3]. Higher energy of carbon ions ($>$ 200 eV) can reduce the compressive stress, thus adhesion is improved, which is correlated to the transformation of sp^3 to sp^2 bonding [3]. In order to control the incident ion energy, a negatively dc or pulse bias voltage was applied to the substrate [4]. The understanding of its effect on the film properties is of technological importance [5,6].

A broad range of surface sensitive techniques [5–10] have been used to characterize the interface morphology of an a-C film on a crystalline substrate. However, the information obtained from these techniques are qualitative. Following to the fact that ion scattering is extremely sensitive to the top most atomic layer, MeV He ion beam backscattering was used in this work as a means of studying the interface morphology of a thin a-C film on a single crystal silicon (100) substrate in a non-destructive manner. The channeling phenomenon of He ions along the <100> axial direction of the Si substrate is utilized in order to highlight the surface peak, which is sensitive to the degree

of disorder of Si atoms around the subsurface region. Thus, this surface peak reflects the situation at the *a*-C layer/substrate interface, which is in turn related to the electrical bias to the Si substrate. Moreover, channeling phenomenon is used to suppress the background intensity of Si backscattering so that backscattering yield from C target is sufficiently well resolved to analyze the peak area. Therefore, the ion channeling measurement has advantage over those techniques especially in its quantitative reliability.

2 Experimental

2.1 Sample preparation

Amorphous carbon films were fabricated by filtered cathodic vacuum arc (FCVA) plasma at room temperature where the carbon plasma was obtained from a 99.995% pure graphite cathode. The FCVA system has been described in detail elsewhere [11]. In brief, the FCVA source was operated in pulse mode based on 10-sections of pulse forming network (PFN) with pulse duration of about 120 s and pulse arc current exceeding 200 A depending on charging voltage to PFN [12]. This experimental pulse arc current was kept at about 572 A with a repetition rate of 2 pps for all samples made. *P*-type Si (100) wafers were used as substrates. Prior to depositing *a*-C films, the substrates were cleaned by following the standard RCA procedure [13]. A dc bias voltage (V_b) ranging from -0.2 to -2.0 kV were applied to the substrate holder during deposition in order to increase the incident ion energy. A solenoid filter was used to remove macroparticles. The energy of carbon ions (in eV) was directly related to the bias voltage (in V) because only singly charged carbon ions were

in the plasma. The substrate holder was placed at about 15 cm from an exit of the filter. The vacuum chamber was evacuated to a base pressure of about 6×10^{-6} mbar by a cryogenic pump.

2.2 Backscattering measurements

The interface morphology of thin *a*-C films was investigated by means of Rutherford backscattering spectrometry in the channeling mode (abbreviated as RBS/C hereafter) [14,15]. The analysis was performed utilizing 2.1-MeV He^{2+} beam produced by the 1.7-MV Tandetron accelerator at Chiang Mai University. The typical ion beam current on the sample was 15 nA. A maximum beam divergence was less than 0.05° with a diameter of 1 mm. Two small permanent magnets were placed in parallel in front of the sample holder for acting as a secondary electron suppressor, enabling accurate monitoring of ion beam charge on the sample. Backscattered He^{2+}-ions were detected by a standard silicon surface barrier (SSB) detector with an energy resolution of 12 keV positioned at 115° with respect to the beam direction. For the channeling measurements, the samples were mounted on a goniometer with two tilting axes which were automatically adjusted in both angles by a computer-based control until a minimum in the axial channeling yield was observed. In order to avoid crystal or film damage due to the analyzing beam, a fresh spot was chosen after each searching procedure. The measuring period of all the RBS/C spectra was controlled by keeping the same value of total He^{2+} charge accumulation on each target in order to reduce the influence of the He^{2+} bombarding fluence on the dechanneling.

3 Results and discussions

Typical 2.1 MeV random and aligned RBS spectra from the as-grown a-C thin film on the Si (100) substrate are shown in Fig. 1. The channeling phenomenon allows us to see the nonshadowed Si atoms of the surface layer more clearly since ions scattered by these atoms appear as a surface peak while those crystalline atoms underneath are almost hidden. This effect also enhances the C-peak that comes from the deposited layer of a-C on top of the Si surface. As shown in Fig. 1, the clarity of the C-peak is far better in the aligned spectrum than in the random spectrum. Quantitative evaluation is possible only from the aligned spectrum.

3.1 Interface disorder, qualitative analysis

In Fig. 2, the ion channeling spectra obtained from a-C thin films deposited on Si(100) wafers are compared for different bias voltages. In this case, the surface peaks around channel number 516 reflect the distribution of those non-shadowed Si atoms. As seen here, the Si surface peaks are increased both in width and height with the substrate bias voltage. The increment of this surface peak is related to the increasing number of displaced Si atoms at around the top layer of Si substrate since major lattice damage builds up in the substrate with increasing irradiation energy. For the first period of deposition, energetic C^+-ions of a few keV can effectively induce displacement of the Si atoms from their original lattice sites due to a low displacement energy of about 38 eV [16]. It is noticed that the front edges of the Si surface peaks slightly shift to lower energy. This fact will be discussed later and utilized for calculation of

the film thickness.

3.2 Oxide analysis

Prior to quantitative analysis of the interface disorder, the surface oxidation situation must be first clarified as surface oxide would affect the Si surface peak of the aligned spectrum. From Fig. 2, no apparent oxygen peak was observed at around channel 355. This could be an indication of a native oxide (SiO_2) free surface of the substrate. The oxide might have successfully been removed following the HF dip. We confirmed this assumption by using the non-Rutherford scattering cross-section effect in the $^{16}O(\alpha,\alpha)^{16}O$ reaction to enhance O-backscattering yield. The deviations of the scattering cross-section from the Rutherford formula are observed for He ion energies above 2.25 MeV scattered from oxygen atoms [17]. There are resonances at 2.5 MeV and 3.05 MeV. Prior to ion scattering measurements, an energy scan was conducted in order to calibrate the He^{2+}-ion energy to the centroid of the $^{16}O(\alpha,\alpha)^{16}O$ 3.05 MeV nuclear resonance via the oxygen signal from an alumina (Al_2O_3) sample. This effect is demonstrated in Fig. 3 for the oxygen peak measured at 3.05 MeV using not cleaned and cleaned Si wafers with the treatment mentioned earlier. The oxygen peak is clearly visible, at resonance energy, only from not cleaned Si. The two spectra of not cleaned sample shown in Fig. 3 correspond to the same sample measured at the resonant energy 3.05 MeV and at about 15 keV off resonance. The sensitivity of RBS to oxygen in the not cleaned sample can be further enhanced by a factor of about 15 due to a higher cross-section than given by the Rutherford formula at 165° backscattering angle [17]. Thus, it is certain that those Si surface peaks are corresponding only to Si atoms at

around the outermost layers of the clean Si crystal or the disordered a-C/Si interface.

3.3 *Interface disorder as a function of deposition bias voltage, quantitative analysis*

To understand the measurement collected in the context of disorder distribution, we provide a brief description of some basic channeling concept. In the framework of the two-beam approximation model [18,19], the normalized yield at depth x, $\chi(x)$, is given by [14]

$$\chi(x) = \chi_R(x) + [1 - \chi_R(x)] \, [N_D(x)/N] \,, \tag{1}$$

where $\chi_R(x)$ is the dechanneled part of the beam, $N_D(x)$ represents the total displaced atom density at depth x and N is the atomic density of the crystal. In this work, the amount of displaced atoms is not too high due to the low irradiation energy. Therefore, it is possible to make a simple estimation to obtain the fraction $\chi_R(x)$ by using the single scattering approximation [14], as approximated by

$$\chi_R(x) = \chi_V(x) + [1 - \chi_V(x)] \, P(x, \psi_{1/2}), \tag{2}$$

where $\chi_V(x)$ is the normalized aligned yield from a virgin crystal and $P(x, \psi_{1/2})$ is the probability that the channeled ions are dechanneled by the disorder in the region between the surface down to the depth x through angles greater than the critical angle $\psi_{1/2}$. By using Eqs. 1 and 2, we can calculate the depth profile of the displaced atoms $N_D(x)$. Conversion from the channel number to the corresponding depth is carried out following the standard procedure

[14,17] based on the geometry of the measurements and the stopping power given by Ziegler [20].

With the method mentioned, the quantitative disorder can be extracted from those RBS/C spectra. Fig. 4 shows displaced Si atom depth profiles as a function of the substrate bias voltage. Gaussian-like disorder profiles are observed. The profile increases both in height and depth into the Si substrate with increasing substrate bias voltage. Also, the total number of displaced Si atoms in the unit area of the disorder profiles in Fig. 4a increases with increasing substrate bias voltage, as shown in Fig. 4b. This fact indicates that the substrate bias voltage is directly associated with the carbon ion energy, as expected, which causes the ions to penetrate deeper and the substrate atoms to have more displacements. The inset of Fig. 4a shows the depth profiles of C-ions and displacement of Si atoms calculated by the Monte Carlo SRIM simulation program [21] for 2-keV C-ions implanted in Si. The distribution of C atoms has nearly a Gaussian shape with a projected range of 9.5 nm while the displacement peak is located closer to the surface at about 4.5 nm with a long damage tail stretching into the whole C distribution region. According to SRIM simulations, the displacement of atoms in the host crystal depends on two factors: the collision between the incident ions and atoms in the host material and the recoil processes of incident ions. The experimental result shows that the position of the displaced atom profile is similar to that of the C distribution; and it can be interpreted that the lattice disorder of Si atoms is mostly due to the implantation of C-ions.

3.4 Carbon film characteristics

By virtue of the RBS/C spectra in Fig. 2, the Si surface peaks are slightly shifted from the surface peak of the clean Si(100) surface towards lower backscattered ion energy due to the energy loss of He^{2+}-ions in traversing the *a*-C front layer. Therefore, the energy difference ΔE between He^{2+}-ions scattered from the surface of clean Si and those scattered from the C/Si interface is related to the thickness of the film. By referring to the known stopping cross section factor and the experimental parameter of the scattering geometry, we can convert the energy difference ΔE to the *a*-C film thickness with the known mass density of the FCVA-deposited *a*-C films [22]. In addition, the C-peaks in RBS/C spectra refer to the carbon atoms from the deposited layer of *a*-C on the Si surface as well as the mixed layer of Si and C caused by the energetic C-ion irradiation. Thus, the total numbers of counts within these C-peaks were considered. The integrated area of the C-peak was evaluated by a straight-line extrapolation of the contribution from the Si substrate. The conversion of measured area to the C film thickness is made by comparison with the height of a random spectrum for Si [14]. From these results, we can estimate the thickness of the intermixed layer, which is the same as the width of the *a*-C/Si interface, from the difference between the total carbon thickness and the *a*-C film thickness.

Fig. 5 shows the width of the *a*-C/Si interface as a function of C^+-ion energy for the total C thickness of about 22 nm. The thickness of the *a*-C/Si interface increases from 0.8 nm at zero bias to 8.9 nm when ion energy is equivalent to 2 keV. This behavior indicates that the width of the *a*-C/Si interface is mainly affected by the carbon ion energy.

To make this point more clear, we compare our results with C^+-ion ranges in virgin Si for the energy range of 0.2-2 keV as calculated by the SRIM simulation program. As shown in Fig. 5, the widths of the *a*-C/Si interface follow the same trend as the ion range although they are all narrower. This is because in a real situation, the incident C^+-ions lose their initial kinetic energy to a greater extent when the carbon layer grows thicker. Thus the C^+-ions enter the Si substrate region with less energy when the carbon irradiation (deposition) time increasing. For example, the C^+-ions, of initial energy 1 keV, can penetrate into the Si substrate to a depth of around 5.7 nm at the most, at the first instant of irradiation. After that the penetration depth continuously decreases to zero within about 3 minutes since the carbon layer has grown thicker than 3.8 nm, which is the range of C^+-ions in carbon film according to SRIM. This behavior indicates that the interface width should be smaller than the ion range, and explains the evidence from Fig. 5 that no significant changes are seen in the interface width of the two different deposition times for the same ion energies.

3.5 Overview of the Si-C interface including total C

To obtain a more quantitative picture of the *a*-C/Si structure, we suggest a model that summarize the experimental observations and our interpretation of the results as shown in Fig. 6 for the V_b = -2 kV case. The depth profile of C atoms was extracted from the C-peak by following the standard procedure [14]. A Gaussian distribution is observed and the total C thickness is obtained from full width at half maximum (FWHM) of the profile. As previously mentioned, the distribution of carbon can be divided into two regions. The first one is the

region where the carbon ions penetrate a certain distance in the Si substrate and knock some of Si atoms out of their bulk lattice position resulting in the interface disorder. The formation of *a*-C/Si interface at the near surface of Si is affected by the energy of carbon ions at the initial stage of growth. The second region is the deposited carbon film on the top of the *a*-C/Si interface. This region represents the *a*-C film. As seen here, the tail of the disorder profile is slightly stretched into the *a*-C film region. This suggests that the Si atoms were "sputtered" by those carbon ions but retained by the thin film on top.

4 Conclusions

The characteristics of the interface between the low-energy FCVA-deposited *a*-C film and the single crystalline Si substrate have been studied in detail with MeV-ion beam analysis, particularly the RBS/C technique. Relevant measurement methods based on the RBS/C spectra have been developed. Quantitative information on the interface and the film has been obtained from the measurements, including the disorder depth profile in the Si substrate, total carbon profile, carbon film thickness and carbon ions penetrated in the interface, which are all in the nano-scale. The overview of the interface that contains the implanted carbon and displaced silicon atoms together with the deposited carbon film shows that the interface expands with increasing of the C-ion energy or the substrate bias voltage.

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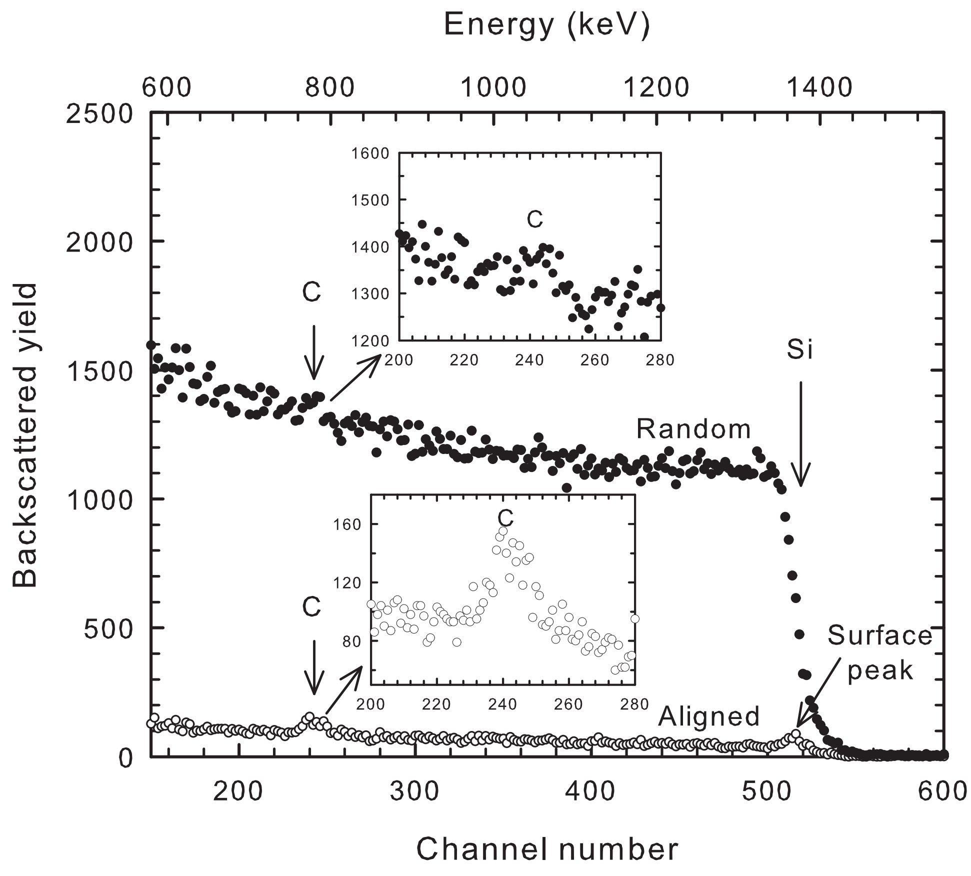

45 Fig. 1. Comparison of random and channeled <100> RBS spectra of the Si(100)
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47 wafer with a 3 nm thick *a*-C film on top. Vertical arrows indicate the expected
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49 position of He^{2+}-ions backscattered from C and Si atoms on the surface. The insets
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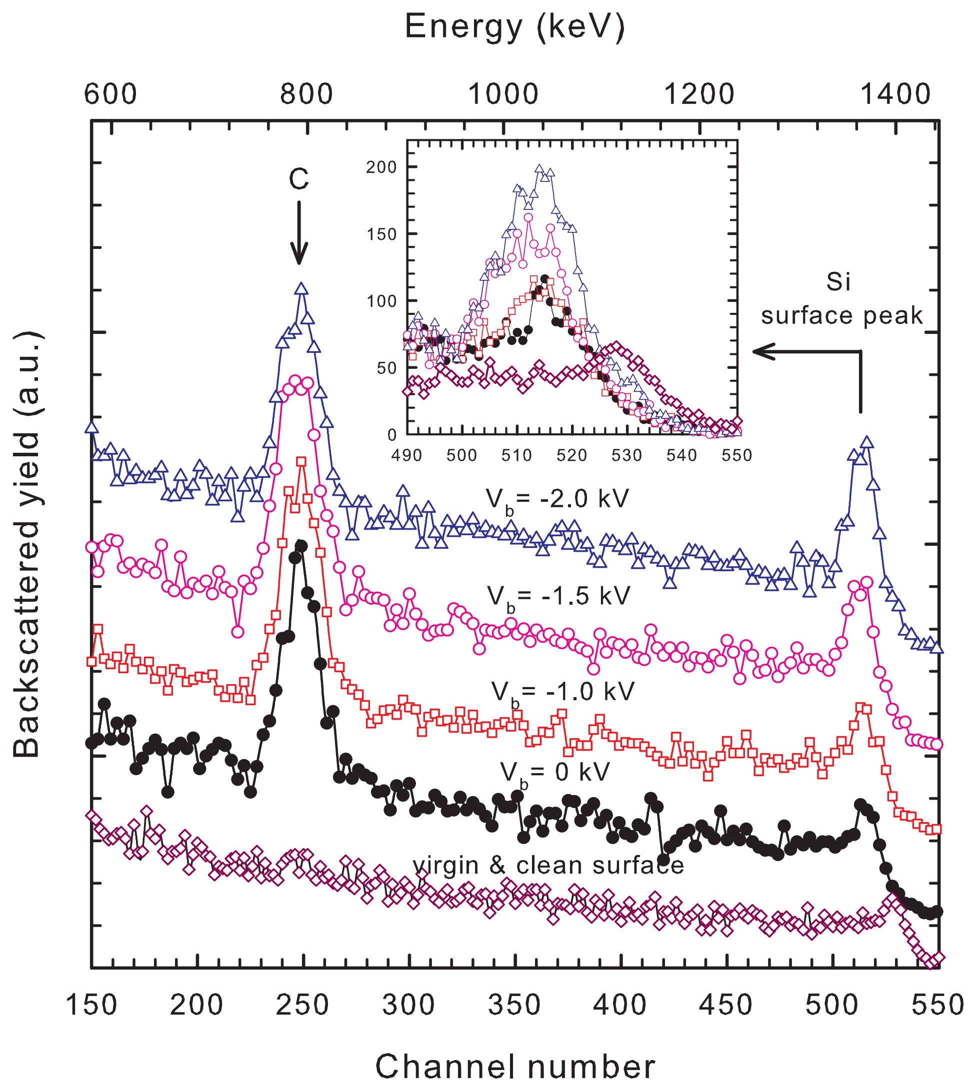

Fig. 2. Measured RBS/C spectra of a 2.1-MeV He^{2+} beam aligned along the <100> axial direction of Si wafers deposited with *a*-C layers at 4 different bias voltages but with the same deposition time. The inset enlarges the Si surface peaks. As a reference, the backscattering yield spectrum along the <100> axis of a virgin Si wafer is also included.

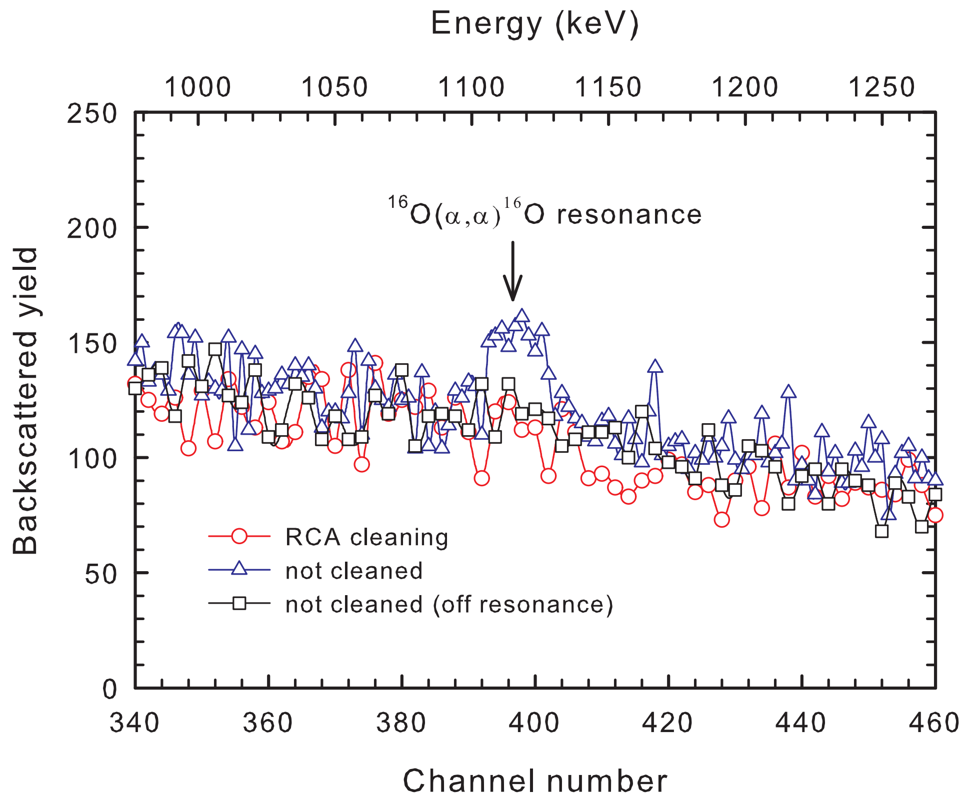

Fig. 3. RBS/C spectra comparing the cleaned and not cleaned silicon wafers at the resonance energy of 3.05 MeV and the same not cleaned sample collected at the about 15 keV off resonance.

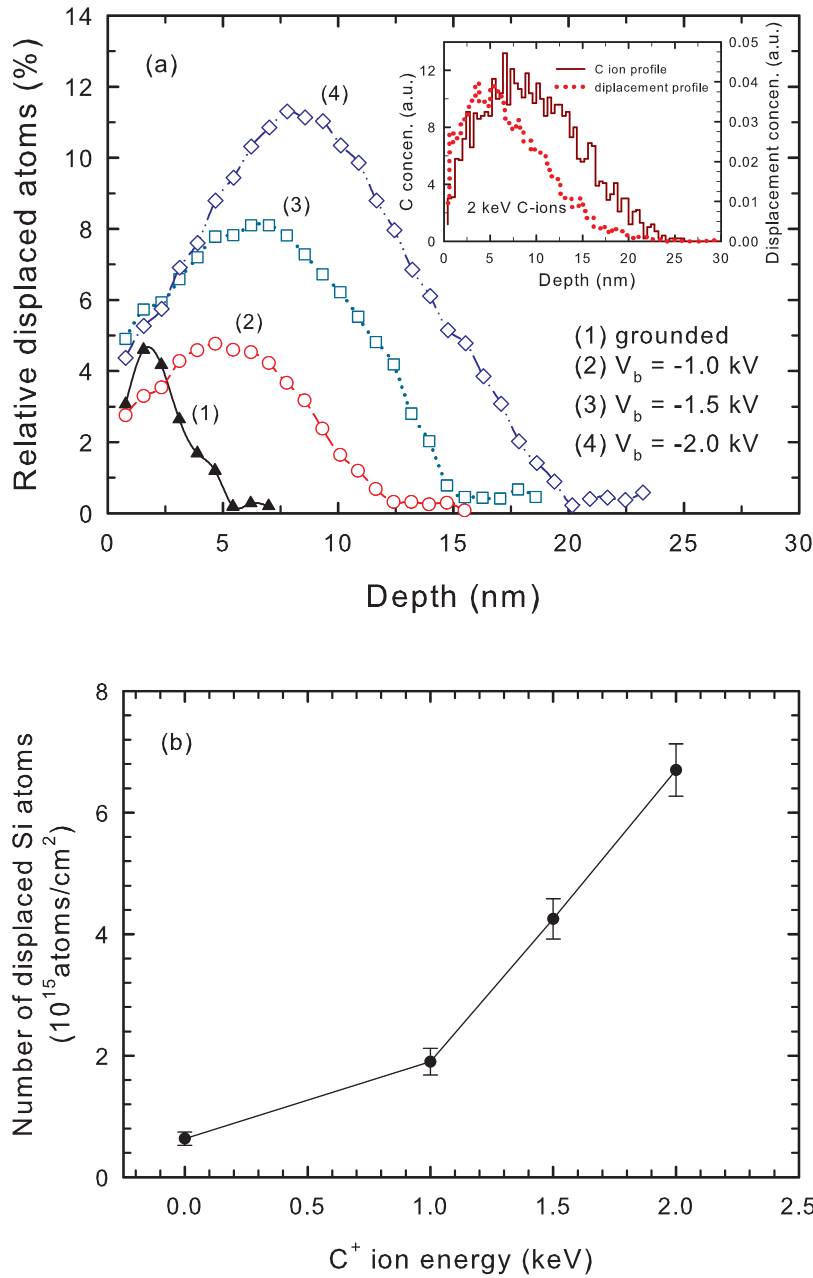

Fig. 4. Analysis of displaced Si atoms as a function of the substrate bias voltage. (a) The measured relative concentration of displaced atoms (N_D/N) in the surface peak of Si wafers deposited with *a*-C layers as a function of substrate bias voltage. The inset shows the C-ion (histogram) and displacement (dotted line) profile for 2 keV C^+-ions calculated by SRIM. (b) The total number of displaced Si atoms in the interface as a function of substrate bias voltage. The solid line is given for reference.

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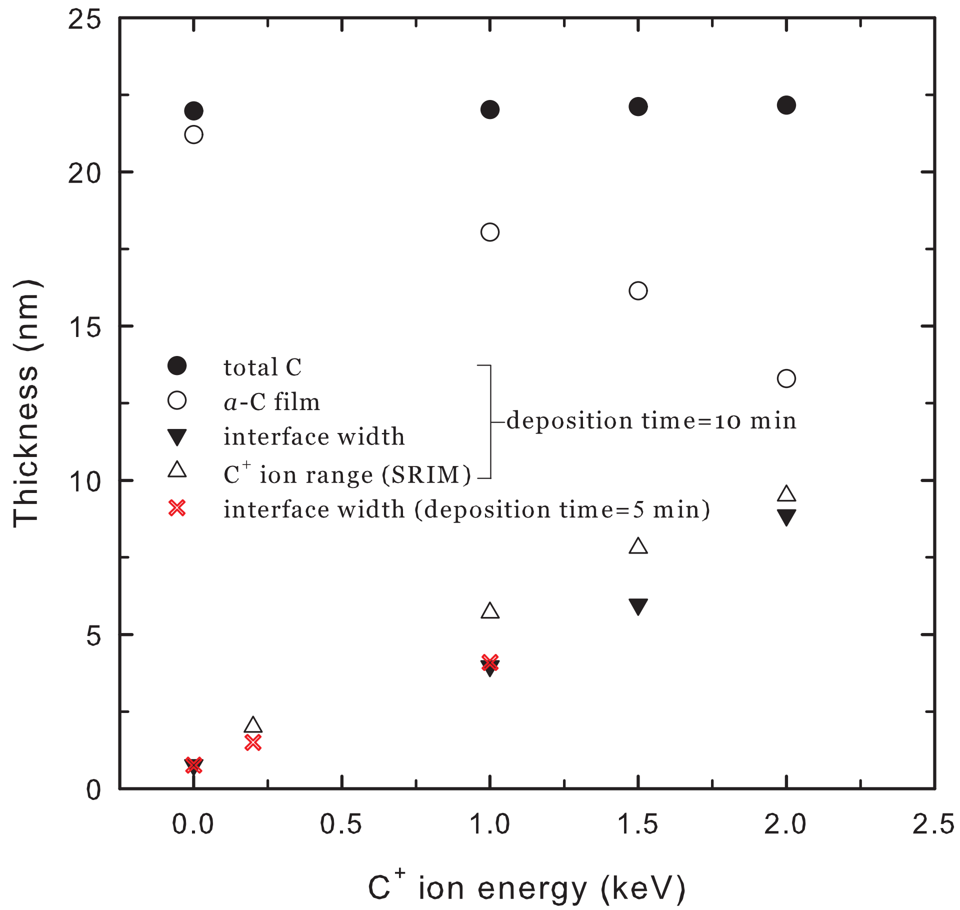

Fig. 5. The thickness of the *a*-C/Si interface and *a*-C film are plotted as a function of C^+-ion energy. The corresponding C^+-ion ranges calculated by SRIM are also included.

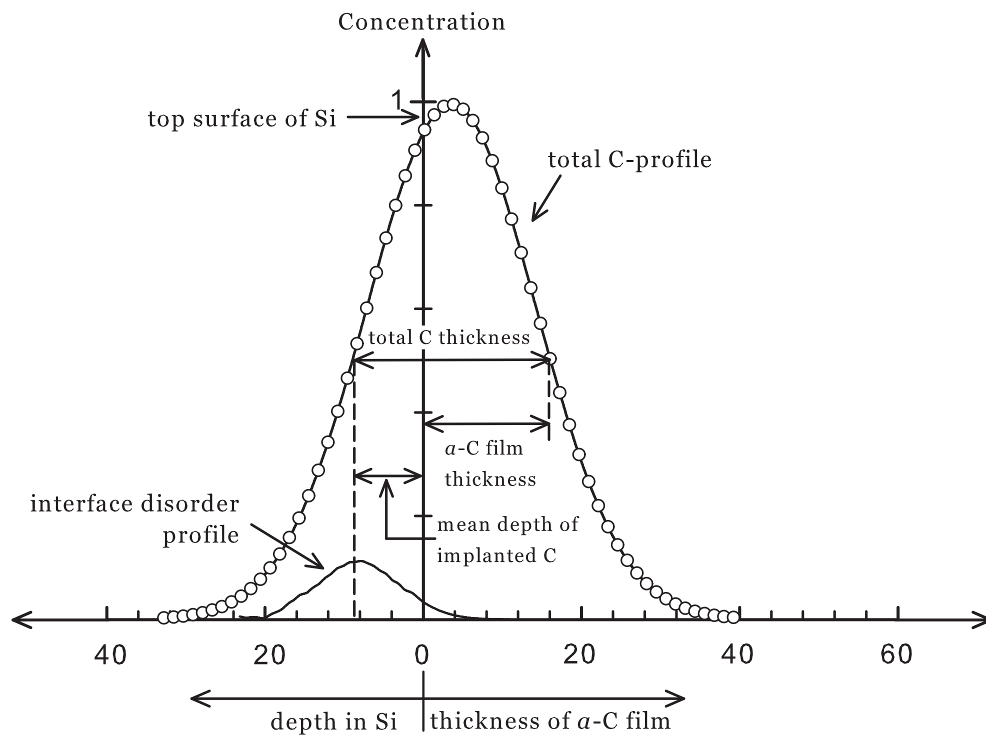

Fig. 6. Overview of a-C/Si interface structure containing the implanted carbon ions and displaced Si atoms together with the deposited a-C film.