

Fracture Behavior of Single-crystal Silicon Microstructure Coated with Stepwise Bias-graded a-C:H Film

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Abstract

Fracture behavior in the tensile testing of a single-crystal silicon (SCS) microstructure with a stepwise bias-graded hydrogenated amorphous carbon (a-C:H) coating was investigated to explore the fracture mechanism of the coating–substrate system. All sides of the SCS microstructure ($120 \times 4 \times 5 \text{ }\mu\text{m}^3$) were coated uniformly with a 300-nm-thick a-C:H film deposited by plasma enhanced chemical vapor deposition (PECVD). In this research, four different bias conditions with stepwise changes were applied during deposition to make the hard–compliant or compliant–hard gradient in the coating film. The microstructure, chemical composition, and mechanical properties were evaluated by scanning electron microscopy, Raman spectroscopy, nanoindentation, and surface profilometry. A tensile test showed a significant increase in tensile strength for samples with a multilayer gradient coating, which was 6.3–56.6 % higher than that of the SCS sample, and a similar increase was observed for fracture toughness. The fracture mechanisms were elaborated by analyzing the chemical composition and stress intensity factor. The results indicate that the tensile behavior was strongly affected by the surface energy and stress state of the a-C:H coating.

Keywords: Tensile testing; Single crystal silicon; Hydrogenated amorphous carbon film; Coating–substrate system; Multilayer gradient coating.

1. Introduction

The mechanical reliability of single crystal silicon (SCS) for applications in MEMS has been widely studied over the last few decades. Investigations of failure behavior, especially the fracture of silicon microstructures, reveal that the brittleness of SCS and the initiation of defects at the interfaces or surfaces are generally responsible for catastrophic failure [1,2], which greatly reduces the mechanical reliability of the microsystem. A protective coating is considered as a straightforward way to solve these problems [3]. In recent years, extensive research has suggested that diamond-like carbon (DLC) films, one of the most advanced film materials, have great potential as protective coatings [4,5]. Hydrogenated amorphous carbon (a-C:H) films are an exceptional subgroup of DLC coatings, which can be deposited by plasma enhanced chemical vapor deposition (PECVD) [4,6]. Such coatings have attracted much attention owing to their desirable properties such as reliable fracture strength and chemical stability [7,8]. Nevertheless, the high internal stress induced by the film growth limits the film thickness since it causes poor adhesion to the substrate, which gives rise to rapid failure or spalling [9-11]. In general, single-side deposition on microscale structure is prone to a destructive warp distortion. Thus, our previous research [12-14] proposed a full a-C:H coating method for free-standing SCS microscale structures deposited by PECVD, and an electrostatic grip system was employed to measure the tensile strength. We found that a single-layer a-C:H coating significantly improves the tensile strength and the torsional fracture strength.

A gradient coating, in which a gradual change in the composition of dissimilar materials is produced by a continuous or layered variation in the depth direction from the bottom substrate to the top surface, can be used to tailor mechanical properties. Compared with a single-layer coating (uniform composition in the depth direction), a gradient coating hinders the propagation of cracks and increases the toughness [15,16]. Since the microstructure of a film is significantly affected by the ion energy during PECVD [17-19], a bias-graded coating formed by a stepwise increase in bias voltage is considered as an effective solution to improve mechanical properties and reduce internal stress [20,21]. Several investigations [10,22,23] reported that the toughness, hardness, residual stress, and adhesion strength are significantly improved with a bias-graded coating. Not by achieving the desired properties through the film growth mechanisms and process optimisation to form more dense and stable coating materials [24,25], but by innovatively redesigning structure can be achieved, which may lead to new applications. In this research, we focus on the tensile behavior

of silicon microstructures with gradient protective coatings, which have not been investigated previously to the best of our knowledge. To fabricate a coating–substrate system with an ideal combination of high strength and toughness, a detailed analysis and discussion of the fracture mechanism of such a microscale structure are of great significance.

In this research, the effects of SCS microstructures with a stepwise gradient coating on enhancing the reliability of fracture behavior were examined. Bias-graded a-C:H multilayer coatings with a compliant–hard or hard–compliant gradient (bias voltage ranging from -200 to -600 V or -600 to -200 V of bias voltage) were prepared by PECVD. Tensile strength was measured using a quasi-static tensile testing system. The effects of the introduced gradient in four different structures of an a-C:H/Si system on the tensile strength, microstructure, and fracture toughness were investigated. The mechanisms for the change in the properties change of these samples were also discussed.

2. Experiment

2.1. Sample fabrication

SCS microstructures (Fig. 1(a)) with a gauge part ($120\text{ }\mu\text{m}$ length, $4\text{ }\mu\text{m}$ width and $5\text{ }\mu\text{m}$ height) were fabricated on a silicon-on-insulator (SOI) wafer ($5\text{ }\mu\text{m}$ Si, $1\text{ }\mu\text{m}$ SiO₂, and $400\text{ }\mu\text{m}$ Si) using a standard MEMS fabrication process (for detail of fabrication, see reference [13]). The surface orientation of the specimen was (100) and the tensile axis was designed to be in the $\{110\}$ direction. An a-C:H multilayer was deposited on a microbeam using PECVD equipment (Shinkoseiki ACV-1060) equipped with a rotation system that can achieve a full side coating. Chips containing 64 tensile-testing specimens were fixed on a jig with an opening window at the center as shown in Fig. 1(b), exposing both their sides to plasma, and the specimens were rotated on their axis while the jig revolved. The rotation rate of the jig was controlled to 4 s/cycle since a higher rotation rate allows sufficiently homogeneous coatings to be formed on each side of the specimens. Before deposition, the chamber was evacuated to a base pressure of 9.5×10^{-4} Pa. To proceed, argon was introduced at a flowrate of 10 sccm and a bias voltage of -400 V was applied for 1 min to clean the specimens. At the beginning of the deposition process, an intermediate SiC layer with a thickness of 20 nm was introduced to improve the adhesion between the coating and SCS substrate. Then, a mixed gas flow of 150 sccm acetylene and 10 sccm hydrogen was introduced. Under the bombardment of plasma, a-C:H film was formed on the surface of the microstructure. As an example, the deposition of a three-layer stepwise gradient film was typically divided into three steps: the bias voltage was first

set to -200 V and the C_2H_2 ions diffused in surface layers, forming a soft initial surface, then the bias stage was increased to -400 V and finally to -600 V with the same deposition time of 60 s for each step. The other three gradient coatings were deposited in a similar manner but changing the number of layers and increasing or decreasing the bias voltage, as illustrated in Fig. 1(c). The four bias-graded samples were named G1, G2, G3, and G4. For easier identification in the following discussion, G1 and G3 are referred to as the compliant–hard group, while G2 and G4 are referred to as the hard–compliant group. A single layer coating deposited with a bias voltage of -400 V named S400 was also fabricated for comparison since it exhibited the highest tensile strength in our previous research [13]. In addition, thin films were also deposited with the same condition on a bare (100) silicon surface for subsequent characterization. Table 1 summarizes the target total and single layer thicknesses, as well as the numbers of layers of coated samples.

2.2. Measurements and characterization

The coated structures were investigated by Raman spectroscopy (Horiba LabRAM-HR800) characterized with a Raman shift in the range of $300\text{--}2200\text{ cm}^{-1}$ with a laser excitation wavelength of 488 nm. The hardness (H) and elastic modulus (E) of the films were investigated with a nanoindenter (Elionix ENT-2100) and calculated with the Oliver–Pharr equation. The maximum load was chosen as 0.4 mN to minimize the effect of the silicon substrate. Average values were obtained by five repeated indentations on different positions, which allowed 15 crack lengths to be evaluated. A surface profilometer (Veeco DektakXT-S) was used to measure the radius of curvature and thickness of the a-C:H films. The residual stress was calculated using the Stoney’s formula [26]. Tensile testing was carried out on a custom-made quasi-static tensile test system at room temperature with a loading speed of $0.75\text{ }\mu\text{m/s}$ (for detail of tensile test, see reference [12]). Twenty samples from at least four different chips were tested for each deposition condition. Niihara’s formula, which is appropriate for small cracks [27,28], was employed to calculate the fracture toughness of the coating–substrate system as:

$$K_c = A \left(\frac{E}{H} \right)^{2/5} \frac{P}{L^{3/2}}, \quad (1)$$

where E and H are the elastic modulus and hardness, respectively, P is the indentation load, and L is the crack length measured from the center of the indented area to the crack tip. A is an empirical constant that depends on the indenter.

Four loads of 25 mN, 50 mN, 75 mN, and 100 mN as well as their corresponding crack lengths were chosen to calculate average values of $P/L^{1.5}$. The crack length after nanoindentation and the cross-sectional structure of the coated gauge parts were characterized by field-emission scanning electron microscopy (FESEM, Hitachi SU-8020).

3. Experiment results

3.1. Raman spectra

Raman spectra of the single-layer film deposited at -400 V and stepwise multilayer a-C:H films with various gradient structures are depicted in Fig. 2(a). A silicon peak was observed at around 520 cm^{-1} , which reveals that the detection depth reached the silicon substrate. Thus, the spectra reveal the comprehensive chemical composition of the entire coating. A broad band at around 1500 cm^{-1} was also observed, indicating the amorphous structure of the gradient layer [8]. For a clear comparison of the decomposed D and G peaks, the spectra of G1 and S400 from 1100 to 1800 cm^{-1} , which are fitted with a Lorentzian model and a Breit–Wigner–Fano (BWF) model, respectively, are depicted in Fig. 2(b). The ratio of the D peak intensity to the G peak intensity (I_D/I_G), showing a strong relationship with sp^2/sp^3 (here we considered that the sp^2/sp^3 can be represented by I_D/I_G , since a similar tendency between I_D/I_G and sp^2/sp^3 was reported in our previous work, see reference [13] for detail), and the ratio k/I_G (hydrogen content), interpreted as the photoluminescent background gradient of the G peak intensity, were calculated from the D peak, G peak, and slope k . Table 2 summarizes the fitting parameters. For the stepwise gradient films, since the thickness of the -200 V layer in the three-layers coating (100 nm, G1, G2) was greater than that in the five-layers coating (60 nm, G3, G4), there was more hydrogen in G1 and G2. Thus, k/I_G value decreased with increasing number of layers. Specifically, although the lowest sp^3 content was measured in the -200 V layer, the existence of a -600 V layer could also densify the a-C:H films and lead to a higher content of sp^3 phases. As a result, the average sp^2/sp^3 ratio of gradient films was slightly lower than that of the single-layer film (S400) deposited with a constant voltage of -400 V. Cai et al. [10] and Shi et al. [22] also reported the same observation. Moreover, in the compliant–hard group (G1, G3), the as-deposited -400 V layer was further bombarded and enhanced by the subsequent deposition of carbon ions with a bias of -600 V, which may increase the sp^3 content, leading to a lower sp^2/sp^3 ratio for the compliant–hard group than for the hard–compliant group (G2, G4).

3.2. Nanoindentation

The force–depth curves of typical indentations are displayed in Fig. 3. The maximum penetration depth was controlled to around 20% of the total a-C:H film thickness, resulting in the measured E and H values being those of a mixture of the coating and substrate, and loads of 0.4 mN were used to determine E and H . The measured mechanical properties are shown in Table 3. For a stepwise gradient coating, it was pointed out by Fischer-Cripps [29] that interpretation errors may exist in when properties are extracted from a single layer to a gradient layer, which means that a depth-sensitive indentation perpendicular to an interface can give rise to inaccurate analysis (due to a variation in contact stiffness) when measuring gradient films [16]. It has also been found that the determination of values is affected by the underlying (bottom) layers [30]. Consequently, G1 and G3 with a soft bottom layer showed a lower E and H values, while G2 and G4, whose underlying layers are hard, exhibited higher values. Therefore, in this study, the measurements of E and H are only treated as reference values rather than accurate values.

The fracture toughness of the a-C:H coatings on Si substrates was measured from the nanoindentation test [31], in which crack length was obtained as a function of load (range from 25 mN to 100 mN). According to the images shown in Fig. 4, the coated samples had a smaller crack length than bare silicon samples and no radial cracks, indicating that the a-C:H films prevent crack propagating from the inside to the surface. The fracture toughness of all the coated samples was higher than that of the bare silicon sample, proving that the a-C:H films played an effective role in toughening. The calculated values are shown in Table 3.

3.3. Residual compressive stress

The residual compressive stress, which was introduced by the bombardment of energetic particles during PECVD [8], was higher in the -600 V layer and lower in the -200 V layer [13]. In general, although a SiC interfacial layer was introduced between the coating and the substrate, the mismatch of the two materials could still cause a high residual stress in a single-layer film [32]. However, in the gradient films, the relatively soft layer acted as a buffer zone, which is susceptible to large plastic deformation, thus eliminating the stress on the surface [33]. As a result, the average stress level of the gradient film markedly decreased compared with that of the single-layer films. Although compressive stress can provide a resistance in the tensile process against the external tensile force,

the difference between different transition of gradient is small (see Table 3). Thus, the effect of compression stress may be negligible, or we prefer to consider that measuring precise values of tensile strength based on compressive stress experimentally is more expedient.

3.4. Tensile test

Typical tensile force–stage displacement curves are depicted in Fig. 5. The bare silicon sample and all the coated samples exhibited the same response with perfectly linear plots. The abrupt decrease indicates that the crack quickly penetrated throughout the entire beam structure, causing catastrophic fracture. The higher applied force at which this occurred showed the protective effect of the a-C:H coating.

Fig. 6 shows the tensile strength of the bare Si sample as well as those of the a-C:H coated samples. Although the E and H values of the coated samples were lower than silicon, a significant increase in tensile strength (6.3–56.6%) was observed. The high values may be attributed to two causes. The first one is that a-C:H coatings can shield and fill the original flaws on the surface of the SOI wafer, which can prevent fracture. The second one, as reported by Nastasi et al. [31], is that the surface energy, which is the work required to produce two new surfaces during failure, is higher (more energy absorption) in the a-C:H coating than in silicon ((111) plane), causing an enhancement in tensile strength. G1 showed a higher strength than the single-layer coating S400. However, G3, which was from the same compliant–hard group, showed a low strength. Moreover, both G2 and G4 had slightly lower tensile strengths than S400. These results may be caused by differences in the stepwise layered structure, which cause resistance against fracture. The fracture mechanism will be discussed in detail later.

Two-parameter Weibull analysis was conducted in our analysis since it is appropriate for evaluating the strength deviation of brittle materials, whose measured data is widely scattered [34]. Fig. 7 shows Weibull plots of all the samples. It was observed that the a-C:H coated samples had a higher shape parameter (Weibull modulus) than the bare silicon microstructures, indicating little scattering of the measured strength.

From the fracture surfaces depicted in Fig. 8, the fracture sections of bare silicon and G1 were rather straight along the (111) plane without deflection (Figs. 8(c) and 8(f)). At the interface, the coated structure was distinguished clearly. Figs. 8(b) and 8(e) show magnification of the fracture

path at the corner. Most cracks were generated from the corner interfaces, and the fracture surface of the coating had no layered structure, indicating no crack deflection on the coating during rapid propagation. All the fracture surfaces were flat and no spalling was observed along the periphery of the section.

4. Discussion

4.1. Effect of fracture toughness

Fig. 9 shows a comparison of the tensile strength, fracture toughness and elastic modulus of the samples. A high elastic modulus resulted in a higher strength except for G1, which was unexpected (at first, we predicted that the change of tensile strength should be consistent with the elastic modulus, shown as a dashed line in Fig. 9, since a higher stiffness usually means higher tensile strength in tensile tests). However, for fracture toughness, a similar tendency to the tensile strength was observed. Notably, our previous work also reported the same observation, which suggested that the fracture toughness of coating–substrate system may mainly determine the tensile strength [13,14]. The results indicate that the stiffness of the coating may affect the tensile behavior of the coating–substrate system, but there should be other factors, i.e., resistance to crack propagation, that further determine the measured strength, which indicates that when the properties of the film itself are limited, higher strength can still be obtained by designing new structures.

It should be mentioned that the toughness of the specimens in this study was slightly lower than that in our previous research, in which the coating thickness was 150 nm. Substantiated experiments and analysis [35] indicated that the stress gradient that developed during deposition is responsible for the reduction in effective fracture toughness since there is a thickness-dependent effect in front of the crack tip [36]. The thickness-dependent effect indicates that in the stepwise gradient layer, the plastic zone size may be smaller than that of a single and thin layer, which leads to rapid fracture of the whole layer. Thus, when trying to deposit thicker films (more than 300 nm), this effect on toughness needs to be considered.

4.2. Fracture mechanisms of the gradient coatings

At first, it is worth to mention that for the mechanical properties, especially for the toughness and tensile strength, we believe that the final results are mainly determined by the effect of crack initiation and propagation under the loading of external force. Thus, the involved physicochemical

effects, fundamentals concerning the plasma, the vacuum and plasma/surface interaction physics during deposition, are not the focus of our research.

Crack propagation theory is used to support the results of the tensile test in terms of the energy release rate, G [37], which is also interpreted as the crack propagation resistance, R . By analyzing the surface energy γ_s and plastic dissipation energy γ_p of the coatings, G is given as:

$$G = 2(\gamma_s + \gamma_p), \quad (2)$$

Generally, the contribution of the surface energy can be explained by the Griffith concept, which is related to the chemical composition. The plastic deformation is mainly determined by the stress state of the gradient coating, which can be described by using the stress intensity factor (SIF) model. It is suggested that the toughness could be affected not only by chemical composition but also by the gradient structure.

Firstly, according to the Griffith concept, which is based on the basic energy balance, the fracture toughness of a a-C:H film has a strong correlation with the sp^2/sp^3 ratio [31]. The number of surface bonds as well as the bond energy is typically employed to evaluate surface energy values. For a toughness model where two new surfaces are created after fracture, the equation can be given as:

$$K_{IC} = \sqrt{N_{surf} E \epsilon}, \quad (3)$$

where ϵ is the bonding energy between two adjacent atoms, N_{surf} is the density of bonds per unit surface area, roughly taken as $1.23 \times 10^{19} \text{ m}^{-2}$ for the a-C:H, and E is the elastic modulus of the coating. Since the a-C:H film consists of a mixture of sp^2 and sp^3 bonds, the average bonding energy is calculated as:

$$\epsilon_{a-C:H} = F_{sp^3} \epsilon_{sp^3} + F_{sp^2} \epsilon_{sp^2}, \quad (4)$$

where F_{sp^3} and F_{sp^2} are the fraction of sp^3 and sp^2 bonds, respectively. ϵ_{sp^3} and ϵ_{sp^2} represent the sp^3 and sp^2 bond energies with a given value of 368 kJ/mol and 638 kJ/mol, respectively [31]. From the I_D/I_G ratio given in Table 2, the order of fracture toughness is calculated as $S400 > G2 \approx G4 > G1 \approx G3$. However, this is different from the measured results of the tensile strength, where G1 has a greater tensile strength than S400.

The change in SIF during crack propagation (determined by the structure dependence) can be used to discuss the fracture mechanism, especially for multilayer composites [38,39]. In this work, the

stress singularities introduced by the mismatch of the layered structure were investigated. Here, as depicted in Fig. 10(a), we assume that defects first initiate in the coating near the Si/a-C:H interface, since the flaws on the silicon surface can easily introduce defects near the interface during deposition. In addition, the complex stress state and the inhomogeneity of the coatings make it easy for cracks to be generated. To simplify the analysis and facilitate the comparison, the fracture process is divided into two steps, that is, i) cracks are generated perpendicular to the interface through the defects and preferentially propagate into the coating film and ii) the coating film completely fails and eventually leading to the failure of the whole beam; see Fig. 10(d).

Generally, step i) contains two situations, as shown schematically in Fig. 10(b) and 10(c). First, a crack exists inside the layer, with the crack length a less than the coating depth h ; second, a crack exists in the gradient coating with the crack tip reaching an interface.

The stress field at the crack tip can be given as [40]:

$$\sigma_{xx}(0, y) = c_1 \frac{\sigma h^s}{(-y)^s}, \quad (5)$$

where c_1 is a dimensionless factor. The stress singularity exponent, s , can be calculated by two Dundurs parameters α and β [41]. The following equation was proposed by Zak [42]:

$$\cos(s\pi) - 2 \frac{\alpha - \beta}{1 - \beta} (1 - s)^2 + \frac{\alpha - \beta^2}{1 - \beta^2} = 0, \quad (6)$$

where $s = 1/2$ for homogeneous materials. In a plane strain problem, α and β are given as:

$$\alpha = \frac{\bar{E}_1 - \bar{E}_2}{\bar{E}_1 + \bar{E}_2}, \quad \beta = \frac{\mu_1(1 - 2\nu_2) - \mu_2(1 - 2\nu_1)}{2\mu_1(1 - \nu_2) - 2\mu_2(1 - \nu_1)}, \quad (7)$$

where $\bar{E}_i = E_i / (1 - \nu_i^2)$, $i=1,2$ is the plane strain modulus of the layers; E_1 , E_2 and μ_1 , μ_2 are the Young's and shear moduli of two neighboring mismatched layers, respectively. β is typically chosen as $\beta = 0$ [43]. As already found in our previous study [13], both hardness and elastic moduli show a linear dependence of the bias voltage. The calculation of α and the corresponding s of G1 to G4 are based on E values (the E values of -200 V to -600 V were taken as 54 GPa, 63 GPa, 71 GPa, 77 GPa, and 84 GPa, respectively), and the results are shown in Table 4.

When the crack tip is fully inside the layers, the crack state is the same as that in a homogeneous medium. Thus, the classical definition of the SIF is used, with:

$$K_I = \lim_{y \rightarrow 0^-} \{\sqrt{-2\pi y} \sigma_{xx}(0, y)\}, \quad (8)$$

For the crack reaching the interface between mismatched layers, the SIF can be expressed as:

$$K_I = \lim_{y \rightarrow 0^-} \{(-2\pi y)^s \sigma_{xx}(0, y)\}, \quad (9)$$

Generally, the generalized K_I is simplified to the normalized fracture mechanics definition to eliminate the dimensional stress-(length)^s effect. Thus, the normalized SIF as a function of dimensionless crack length a/h is defined as:

$$F(\alpha, \beta, \frac{a}{h}) = \frac{K_I}{\sigma(\pi h)^{1/2}}, \quad (10)$$

In Figs. 11(a) and 11(b), the normalized SIFs of crack-tip are plotted against the normalized crack length a/h . The curve of the homogeneous coating S400 is also plotted for comparison. Only the case of approaching an interface is considered, since the SIF value for termination at an interface becomes infinite in the calculation [44]. The curve indicates that the material mismatch may leading to a singularity effect, where a strong fluctuation can be observed at the interface [45].

In the case of $\alpha > 0$ (hard-compliant group in Fig.11(a)), the SIFs are similar to that of S400, which shows a general increase with a/h . As the crack-tip approaches the interface, the SIF sharply increases, which is immediately followed by a sudden drop at the interface. Since the greater the singularity, the more easily the crack propagates [44], the hard-compliant transition has an anti-shielding effect [46]. Notably, the singularity increases with $|\alpha|$ because the mismatch between each layer increases with $|\alpha|$, as shown in Table 4. In particular, because of the effect of the stepwise structure, the actual crack driving force at the interface will have a destructive impact, being four times stronger in G4 and twice weaker in G2, causing the rapid failure of G4. As a result, the fracture toughness has the order of S400 > G2 > G4.

With regard to $\alpha < 0$ (compliant-hard group), the SIF in Fig.11(b) shows a similar increase with the crack length. In general, when the crack approaches an interface, the SIF decreases, but after crossing the interface, a jump in SIF occurs, showing a crack tip shielding effect [46]. Additionally, this jump increases with $|\alpha|$. G1 has two large jumps, indicating that crack propagation is blocked temporarily at the interface, which results in the higher toughness and strength of G1. In contrast, G3 fits the curve of S400 very well, indicating a weak shielding effect. Hence, once a microcrack is generated, the G3 sample could easily induce catastrophic fracture. In such a rapid failure process,

this low resistance can be ignored. Therefore, the order of $G1 > G3 \approx S400$ is estimated, which suggests that the singularity phenomenon (shielding effect) in the stepwise gradient layers will be weakened when the gradient layers are subdivided into a more continuous distribution. Correspondingly, it can be predicted that if the number of gradient layers is more than five, the shielding effect will further decrease. A similar observation has been reported by Lehoczky et al. [47], who predicted that a strong driving force is required to promote crack growth from low-modulus layers into the high-modulus layers.

By combining the composition and structure dependences, the results of the tensile test can be explained. Additionally, the comparison between the fracture toughnesses of G1 and S400 is consistent with the results of SIF analysis, which indicates that the fracture resistance of the coating is strongly affected by the gradient structure.

Conclusion

In this study, four different gradient a-C:H full coatings (300 nm thickness) were deposited on the surface of an SCS microstructure by stepwise control of the bias voltage during PECVD. The microstructure, mechanical properties and fracture behaviors of coated samples were studied systematically by comparison with a sample deposited at a constant bias of -400 V as well as bare silicon. Generally, the fracture surfaces of all samples exhibited brittle fracture behavior as expected. Compared with the homogeneous coating, performance testing showed similar hardness and elastic modulus values but a low residual stress of the gradient coating. The measured tensile strength of coated microstructure was 6.3–56.6% higher than that of the bare sample. The fracture toughness exhibited a similar tendency and dominated the tensile strength. The sample with three-layer coating and a compliant–hard gradient showed the highest strength and toughness, which is attributed to the high crack propagation resistance. The chemical composition and gradient structure, analyzed by the surface energy and stress state, respectively, were found to jointly explain the tensile behavior of the a-C:H/silicon system. Typically, the sp^2/sp^3 ratio of the gradient coating determined the surface energy, while in the SIF model (used to investigate the stress state of crack propagation), which consisted of layers with a compliant–hard transition, a shielding effect was produced, whereas a hard–compliant transition introduced the anti-shielding effect, causing a variation of the stress state. The results suggested that the number of layers and the gradient transition need to be

carefully selected since these conditions have a major effect on the tensile behavior. We believe that this work provides helpful guidelines for designing gradient protective coating with outstanding mechanical performance.

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Figure Caption

Fig. 1 Sketch of a-C:H coated microstructure. (a) Microstructure with a coated gauge part. The inset figure shows the magnification of the gauge part, which is fully coated by gradient a-C:H film. (b) Rotation system of PECVD machine. (c) Five kinds of coated samples.

Fig. 2. (a) Raman spectra of different films from 250 to 2200 cm^{-1} . (b) Raman spectra of G1 and S400 from 1100 to 1800 cm^{-1} .

Fig. 3 Nanoindentation curve of a-C:H coating.

Fig. 4 Typical indentation cracks with maximum loads of 25 mN and 50 mN.

Fig. 5 Typical tensile force–stage displacement curves.

Fig. 6 Tensile strength of SCS and a-C:H coated microstructures. The dashed line represents the tensile strength of pure silicon sample.

Fig. 7 Weibull plots of SCS and a-C:H coated microstructures.

Fig. 8 Typical fracture surfaces of (a)-(c): Si and (d)-(f): G1. (a) and (d) Fracture section. (b) and (e) Magnified observations of the fracture path at the corner. (c) and (f) Right view of fracture section. [Scale bars = 1 μm].

Fig. 9 Comparison of tensile strength, fracture toughness, and elastic modulus.

Fig. 10 Coating–substrate composite material with a crack. (a) Cracks generated on the coating side close to the interface between the substrate and the coating. (b) Crack tip inside the layer. (c) Crack tip touching the interface. (d) Crack finally propagates into the substrate, causing catastrophic fracture.

Fig.11 Comparison of SIFs during propagation. (a) For $\alpha > 0$ (hard–compliant group). (b) For $\alpha < 0$ (compliant–hard group).

Table list

Table 1 Total thicknesses, single layer thicknesses and numbers of bilayers of the a-C:H samples.

Types	G1	G2	G3	G4	S400
Target total thickness (nm)			300		
Single layer thickness (nm)	100	100	60	60	300
Number of layers	3	3	5	5	1

Table 2 Fitting parameters of Raman spectra of a-C:H films.

Types	I_D	I_G	k	I_D/I_G	$k/I_G \times 10^{-6}$
G1	27580	40179	0.13	0.68	3.23
G2	35136	46518	0.15	0.75	3.22
G3	27194	40709	0.11	0.67	2.70
G4	34024	44109	0.13	0.77	2.94
S400	28983	30928	0.08	0.93	2.58

Table 3 Mechanical properties of SCS and a-C:H films.

Samples	a-C:H film					SCS
	G1	G2	G3	G4	S400	
Thickness/ nm	314	308	315	310	289	—
Elastic modulus/ GPa	53.5	64.2	54.1	63.4	70.4	181.4
Hardness/ GPa	7.44	8.19	7.31	8.29	9.11	13.04
Residual stress/ -GPa	0.402	0.562	0.389	0.546	0.861	—
Toughness /MPa $\sqrt{m}$	1.64	1.41	1.22	1.36	1.56	1.19

Table 4 Crack tip singularity exponent, s , as a function of α for $\beta = 0$

$\beta=0, \alpha / s$	Layer 1	Layer 2	Layer 3	Layer 4
G1	-0.134 / 0.482	-0.0795 / 0.489	—	—
G2	0.0795 / 0.514	0.134 / 0.525	—	—
G3	-0.0764 / 0.489	-0.0579 / 0.492	-0.0398 / 0.494	-0.0399 / 0.494

G4

0.0399 / 0.507

0.0398 / 0.507

0.0579 / 0.511

0.0764 / 0.514

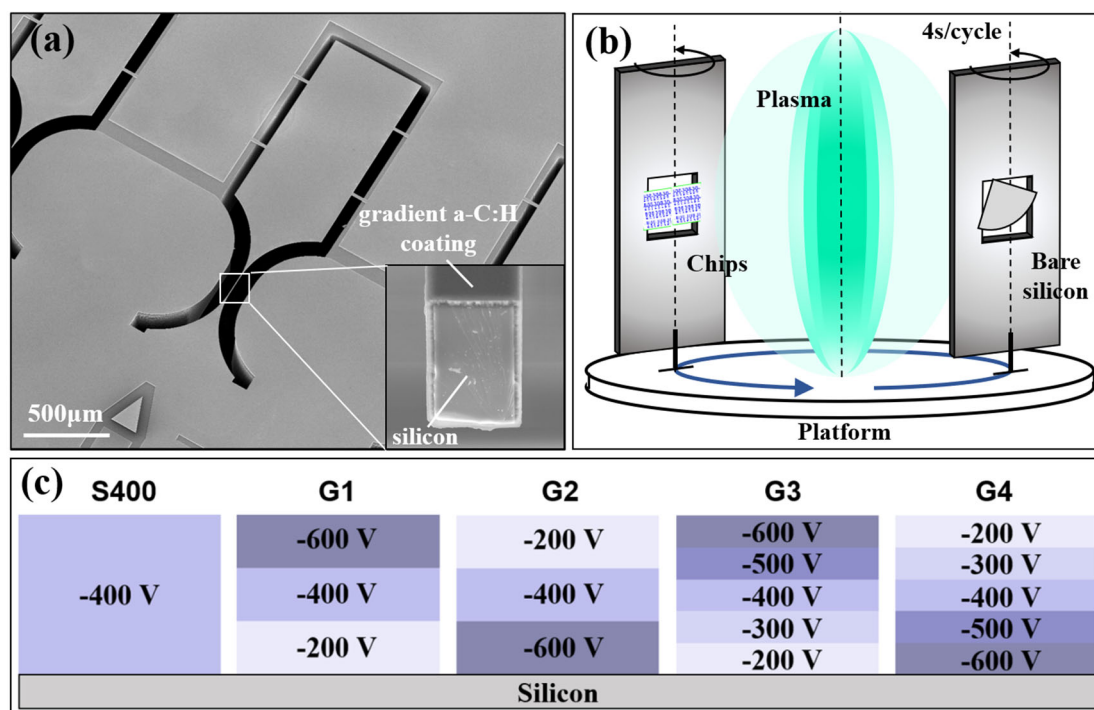


Fig.1

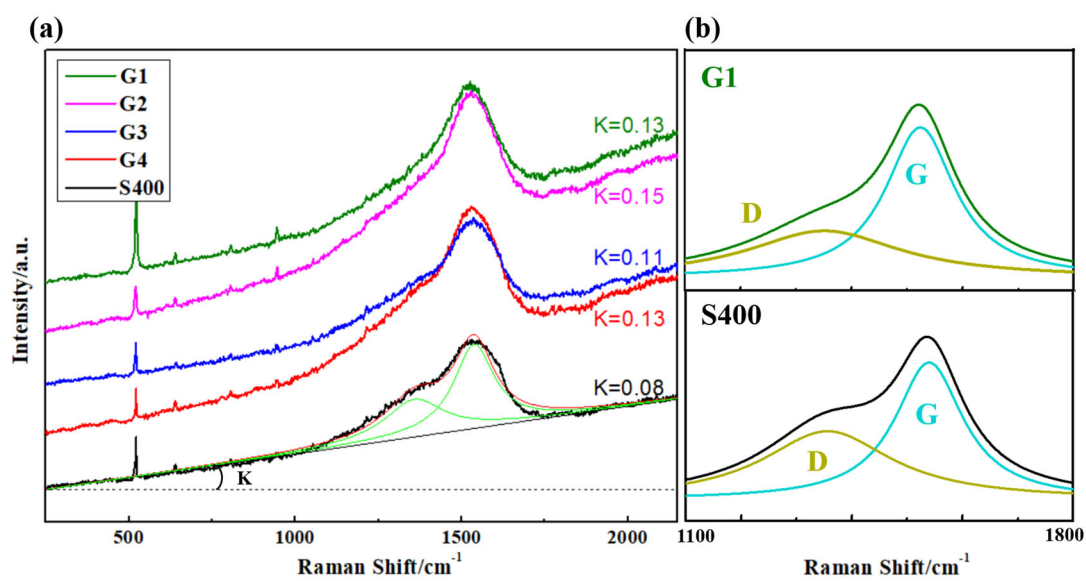


Fig.2

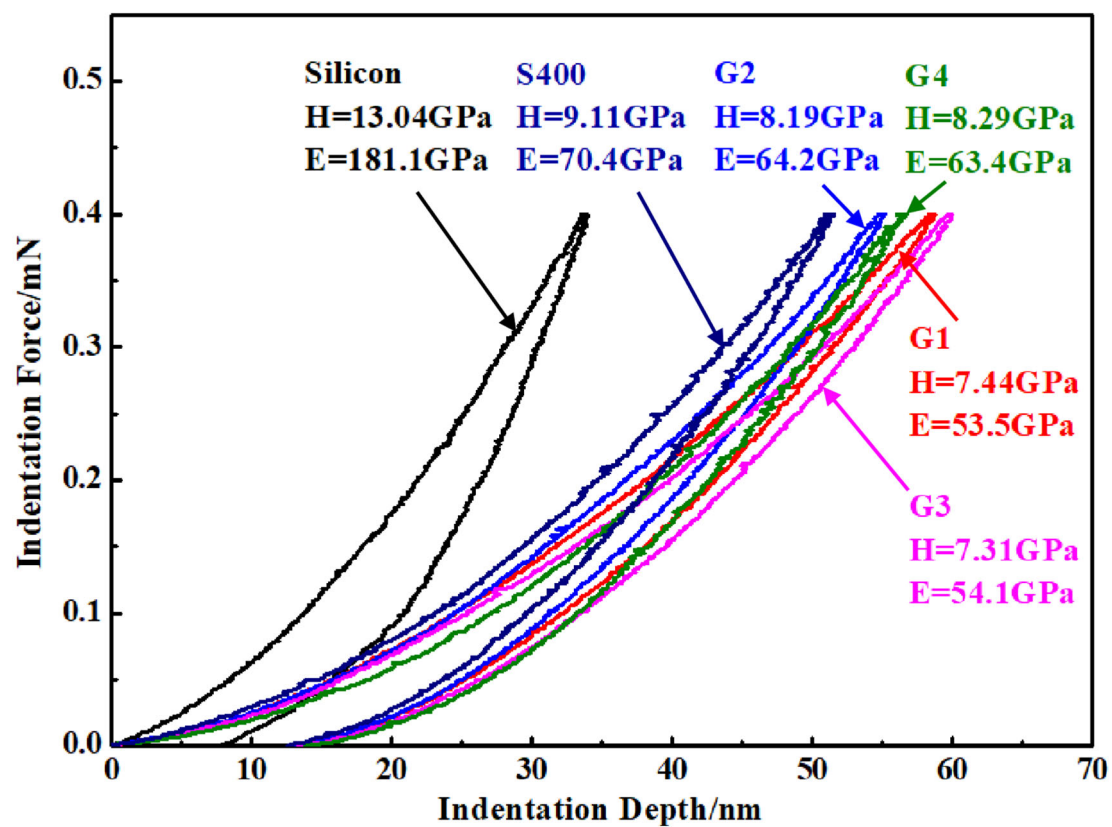


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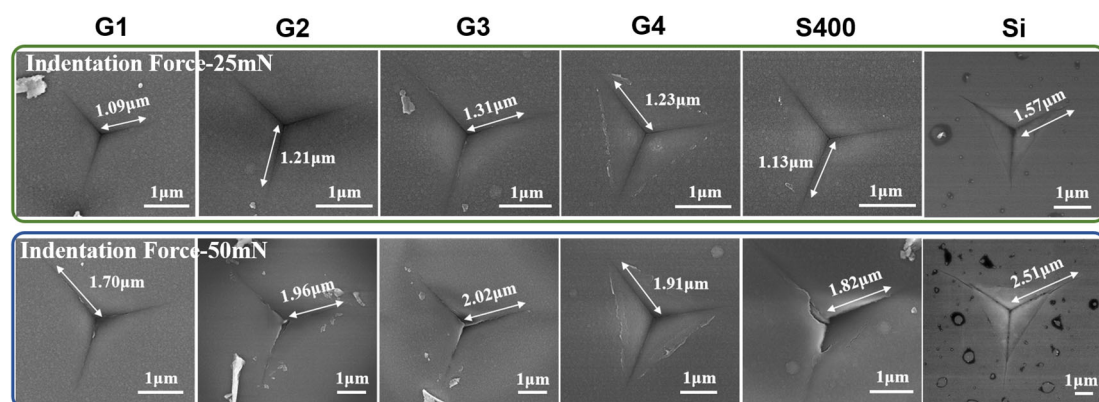


Fig.4

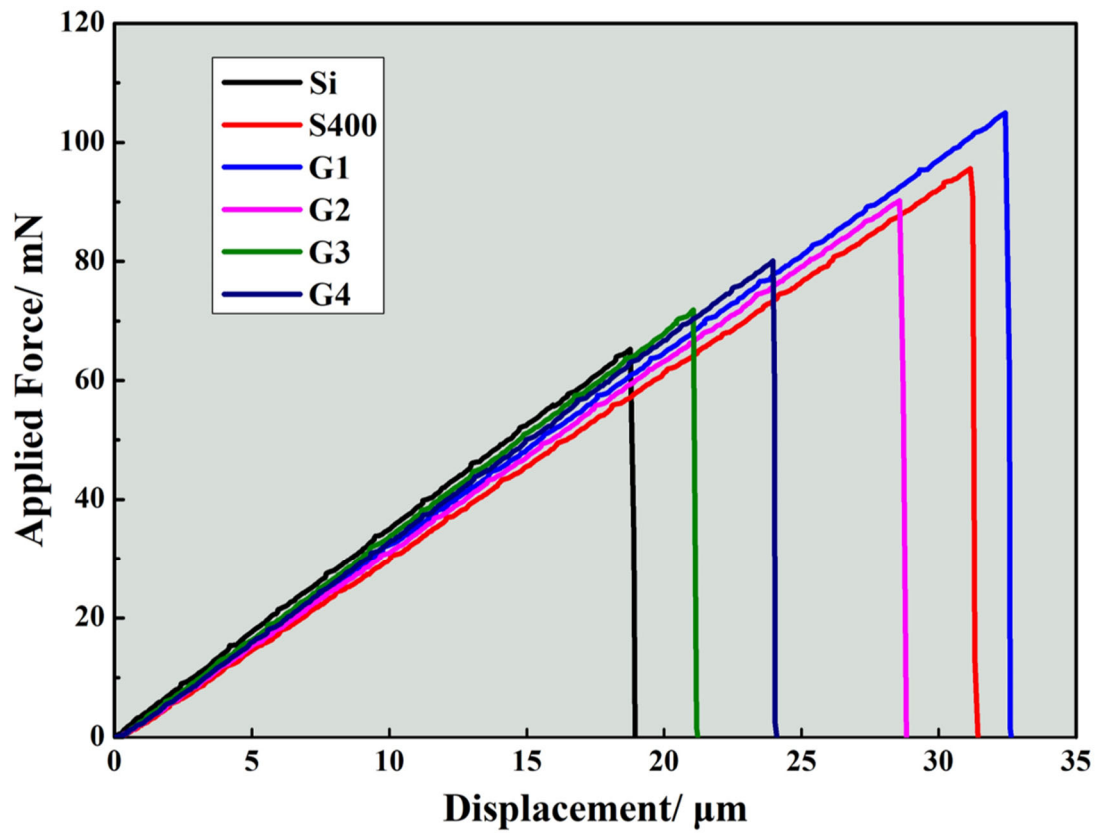


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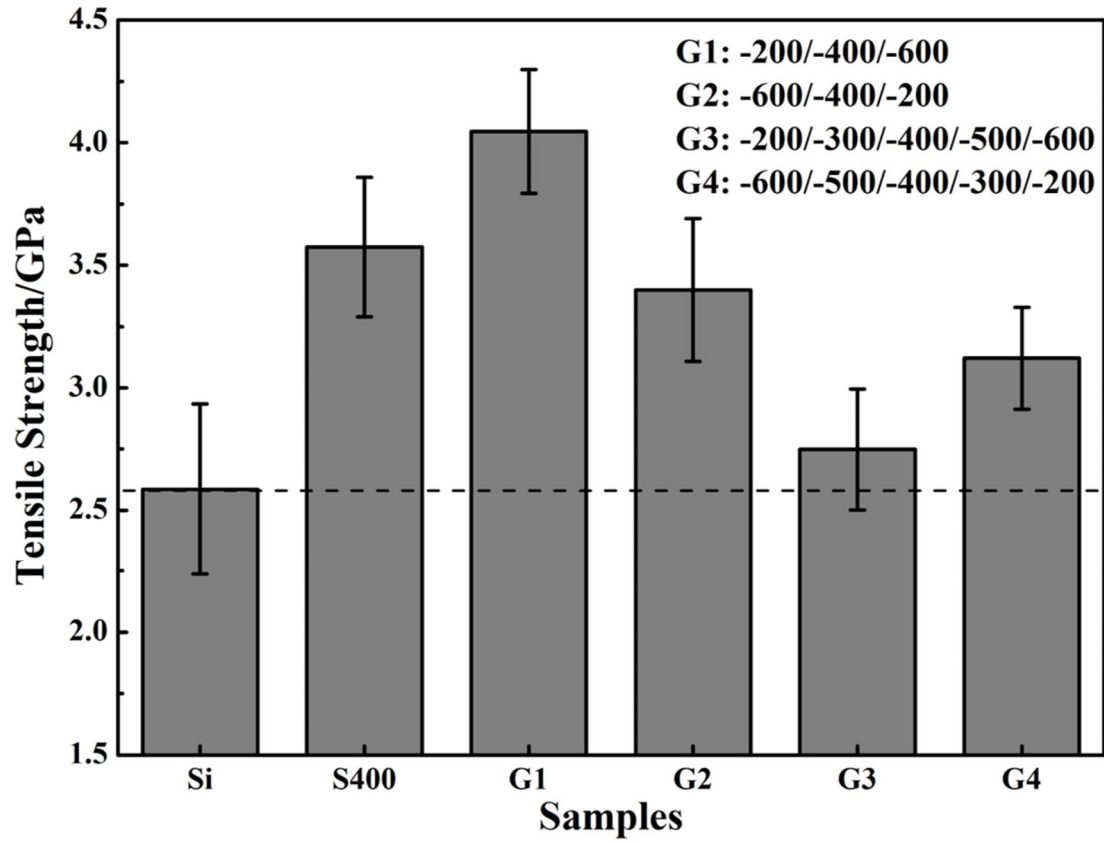


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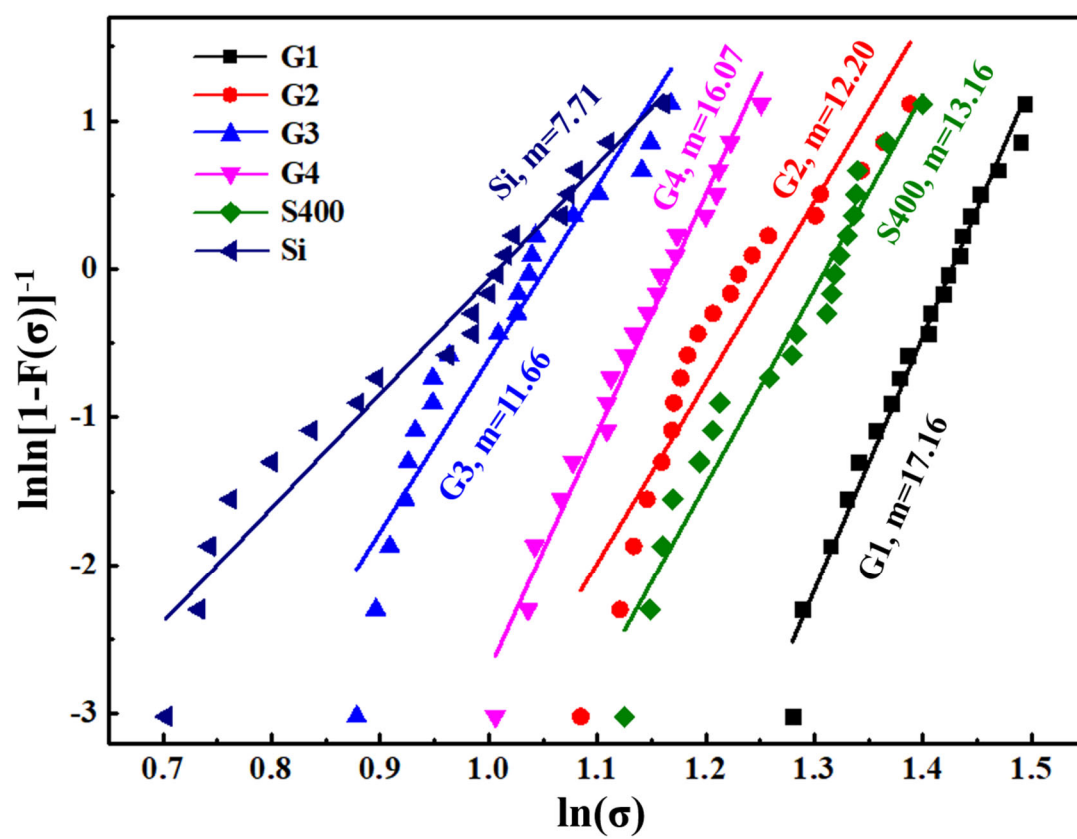


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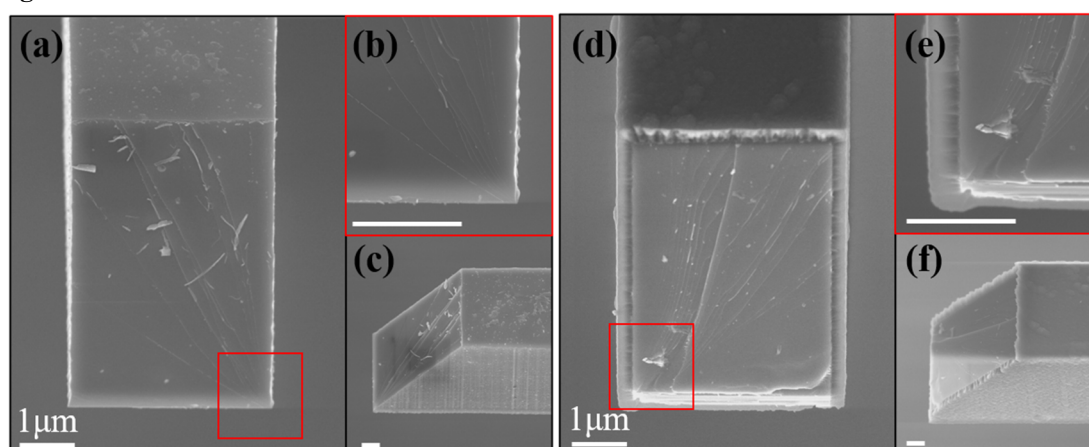


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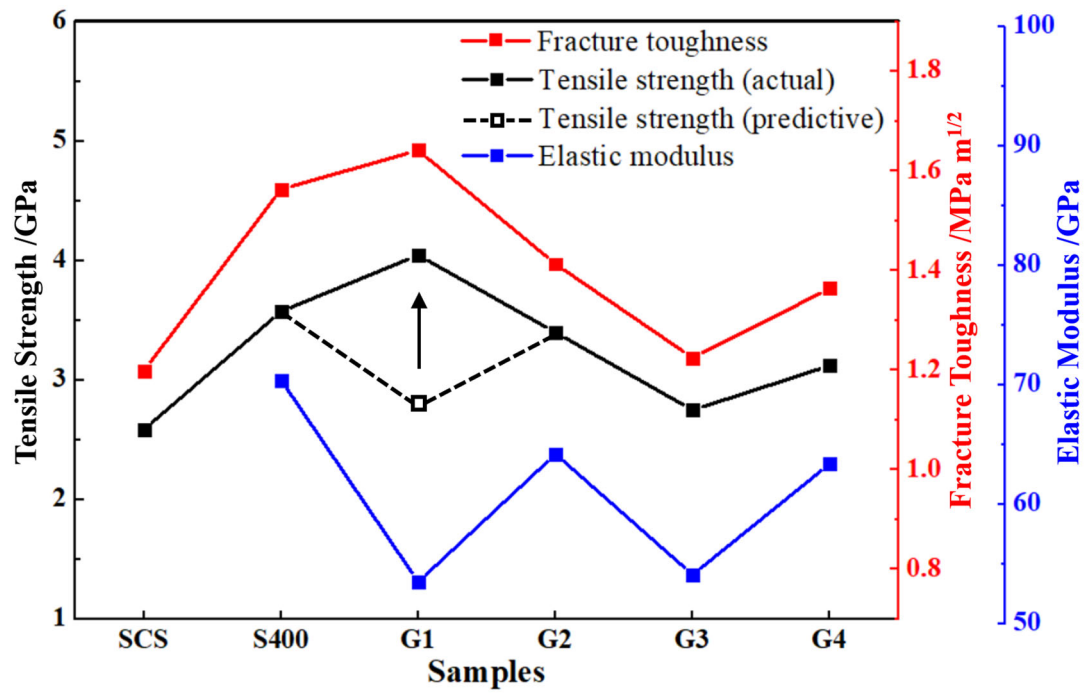


Fig.9

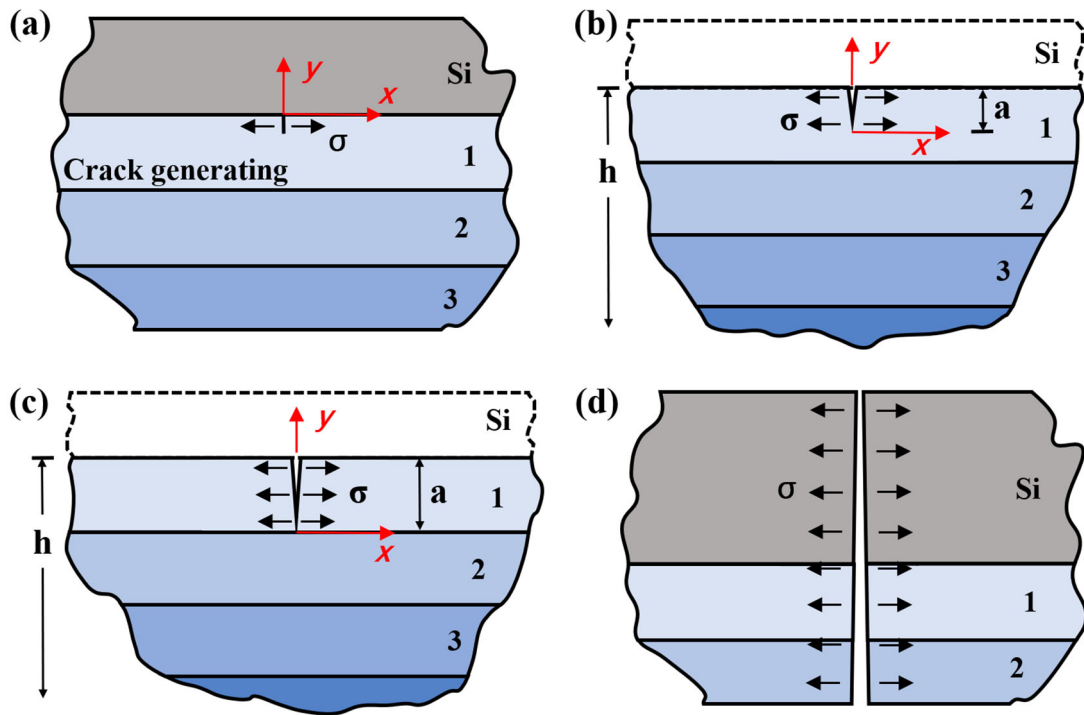


Fig.10

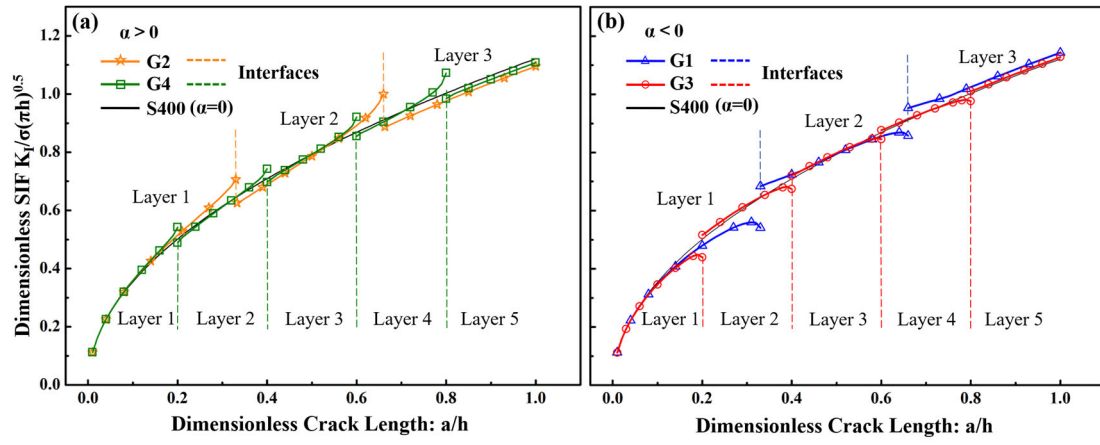


Fig.11