ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 7, № 3 (2006) С. 555-559

PHYSICS AND CHEMISTRY OF SOLID STATE
V. 7, № 3 (2006) P. 555-559

УДК 621.794'4: 546.48'24

ISSN 1729-4428

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Thermal Treatment Effect on the Tin Melt Adhesion to the Surface of Amorphous Silicon Carbide Films

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A comparative study of the effect of the vacuum high-temperature annealing on the amorphous silicon carbide films structure and wettability with tin melt was conducted. Near-stochiometric amorphous silicon carbide films were deposited by two methods: reactive magnetron sputtering of silicon target in Ar+CH_4 gas mixture (a-SiC:H) and by modified vacuum arc deposition using SiC cathode (a-SiC). Capillary properties of the surface were analyzed by the sessile drop method in the temperature range from 250 to 700 °C at a pressure of $1 \cdot 10^{-3}$ Pa. Structures of the films were analyzed using Raman scattering and FTIR absorption spectroscopies. It has been found, that the variations in wettability and adhesion of tin melt to the film surface under annealing correlate with the variations in their structure and chemical state of the surface. For the a-SiC films the structure ordering of a-SiC and formation of SiC nanocrystallites is observed. For the a-SiC:H films dehydrogenation of the structure and the formation of free carbon clusters at 650 °C and above with subsequent surface cleaning at high temperature is seen.

Key words: amorphous silicon carbide films, wettability, adhesion, annealing, structure ordering, ultrathin carbon layer formation.

Стаття поступила до редакції 07.12.2005; прийнята до друку 15.06.2006.

Introduction

Preliminary our experiments have shown that a high-vacuum heat treatment of amorphous silicon carbide films brings about an essential decrease of adhesion of metallic contacts to the film surface. On additional chemical purification of the annealed film surface the metal adhesion is restored. Examination of the film surface using optical and atomic force microscopies does not reveal any changes in the surface morphology up to 800 °C. This suggests that the impairment of adhesion is caused by a change in other surface characteristics. This points to a change of physical-chemical properties of the surface.

The aim of present work is to study in details the effect of thermal treatment on the surface properties of amorphous silicon carbide films, to clarify the reasons for the impairment of the metal adhesion to the surface of vacuum-annealed films. The film surface properties have been studied using capillary method, that is extremely sensitive to interatomic interaction on the interface of film-testing liquid-gas by measuring of contact angle of the liquid drop. In previous papers [1-4] it had been found the high sensitivity of the contact angle to peculiarity of the structure, composition and chemical state of the thin film surface.

I. Experiment

To study the heating effect on the surface capillary properties, we have prepared films of hydrogenated (a-SiC:H) and unhydrogenated (a-SiC) amorphous silicon carbide films of 300 and 100 nm in thickness, respectively, and with the composition close to stoichiometric. The films have been deposited onto n-doped (100) silicon wafers at a substrate temperature of 200 °C and 60 °C, respectively. Two different techniques were used for deposition: reactive dc-magnetron sputtering of silicon in Ar+CH_4 gas mixture (a-SiC:H) and ion-plasma deposition using polycrystalline silicon carbide as a vacuum arc source (a-SiC). The film deposition procedures have been described in detail in [5] and [6]. To study the heating effect on the short-range structure of the films, they have been isochronously annealed in a vacuum of 10^{-4} Pa at a temperature up to

850 °C for 15 min. Structures of the films was analysed using Raman scattering and FTIR absorption spectroscopies.

Tin has been chosen as a liquid phase to study the film wettability. In the temperature range under study tin does not impair the experimental conditions in a vacuum because of the very low elasticity of its vapor (at 1000 °C, the pressure of the saturated tin vapor is $6.67x10^{-3}$ Pa [7]). The effect of the temperature on the surface wettability of *a*-SiC:H and *a*-SiC films with the tin melt has been in situ studied by the sessile drop method (drop diameter has ranged from 0.5 to 0.8 mm) in vacuum $1{\cdot}10^{-3}$ Pa in the temperature range from 250 to 700 °C. We have used an experimental system that includes a vacuum chamber and a device for reading and analysis of the drop optical image. The accuracy of the contact angle measurement was ±1-2°.

II. Results and discussion

1. Chemical composition

Auger electron spectroscopy has shown the following composition: Si (40 at.%), C (55 at.%)55, O (3 at.%), N (2 at.%) for the as-prepared a-SiC:H films and Si (57 at.%), C (41 at.%), O (2 at.%) for the as-prepared *a*-SiC films.

2. Wetting and adhesion

It has been found that at 250 °C the contact angles for the initial a-SiC:H and a-SiC films, despite the quite different morphologies, practically coincide and are respectively 158 and 160° (fig. 1a). As is seen from the figure, the temperature dependences of the wetting angle can be arbitrarily divided into three regions. In the range from 250 to 350 C the contact angles decrease, and for the a-SiC:H film, it decreases more slowly. Between 350 and 600 °C the contact angle of the a-SiC:H films does not practically change and for the a-SiC films decreases slightly (to 148 °C). At temperatures above 600 °C a detectable decrease in the contact angles is observed, though, the contact angle value for the *a*-SiC:H films is higher.

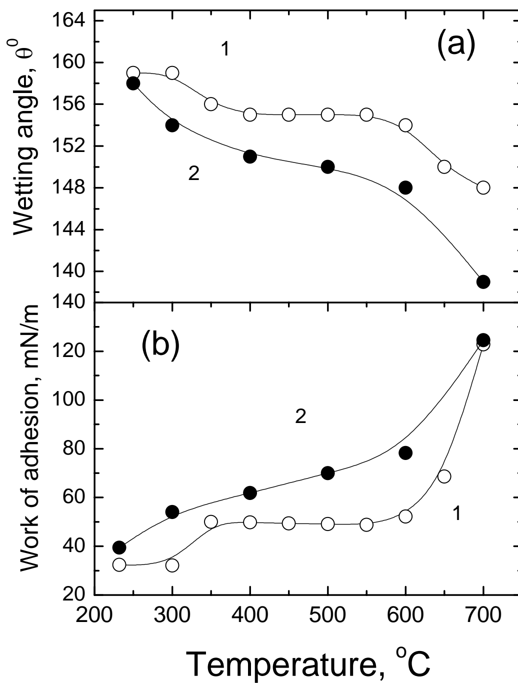

Fig. 1. Temperature dependences of the wettability with tin (a) and the work adhesion (b) for amorphous silicon carbide films: 1 – a-SiC:H and 2 – a-SiC.

Based on the measured values of the contact angle, the work of adhesion, Wa, has been calculated by the expression

$$Wa = \gamma lg\ (1 + \cos\theta), \quad (1)$$

where γlg is the surface energy at the liquid-gas interface.

The work of adhesion is an energy parameter of the interaction between molecules of a liquid and a solid [8]. The higher the work of adhesion, the better a liquid wets the surface of a solid. Figure 1b shows the respective temperature dependences of the work of adhesion for the a-SiC:H and a-SiC films.

3. Structure analysis

The effect of the thermal annealing on the structure relaxation of the amorphous silicon carbide films has been analyzed by FTIR and Raman spectroscopies. Unfortunately, we have failed to measure Raman spectra of the a-SiC films probably due to strong scattering of the laser irradiation by the roughness of the film surface. The absorption band at 800 cm^{-1}, which can be assigned to the vibration of (Si-C) bonds, dominates in the IR spectra of the as deposited a-SiC:H films (Fig. 2, spectrum 1). In addition to this basic band, two additional

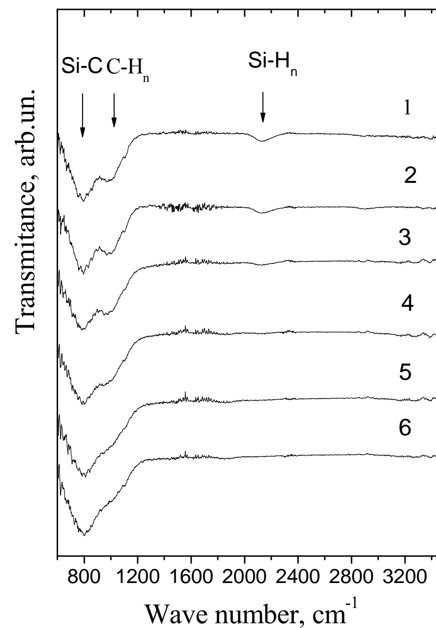

Fig. 2. IR transmission spectra of the a-SiC:H films : 1 – initial film at 20 °C; 2 – 450 °C; 3 – 550 °C; 4 – 650 °C; 5 – 750 °C; 6 – 850 °C.

bands at 1000 and 2100 cm^{-1} are seen in the spectra. The intensive absorption at 1000 cm^{-1} is due to vibrations of hydrogen bonds in structural chains of the Si–C–Hn type.

The absorption at 2100 cm^{-1} might be unambiguously assigned to stretch-vibration mode of Si–Hn bonds. FTIR spectra of the samples after thermal treatment showed that the intensity of the absorption band at 2100 cm^{-1} (fig. 2) monotonically decreased with increasing temperature that is an evidence of breaking of Si-H bonds. After annealing at T>650 °C this band was not detectable at all. At annealing temperature higher then 450 °C absorption band at 1000 cm^{-1} was monotonically decreasing (fig. 2) due to breaking of the carbon-hydrogen bonds.

As deposited and low temperature treated a-SiC:H sample showed no Raman scattering signals. After annealing at T>650 °C weak and very broad band centred about 1420 cm^{-1} appeared in Raman spectra (fig. 3).

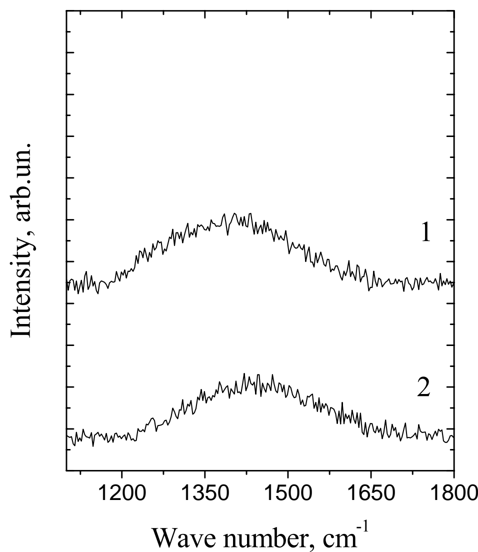

Fig. 3. Raman spectra of the a-SiC:H films annealed in vacuum: 1 – 750 °C; 2 – 850 °C.

This band should be attributed to amorphous carbon clusters [9, 10]. Usually Raman scattering spectra of the amorphous carbon are represented by superposition of two bands, so-called G-band («graphitic», 1500-1600 cm^{-1}) and D-band («disordered», 1300-1400 cm^{-1}). It is generally recognised that the ratio of intensities of D- and G-bands (ID/IG) depend on the carbon cluster size. For the cluster size larger than 1.2-2.5 nm the ID/IG increases as cluster becomes smaller. But for crystallites smaller than 1.2-2.5 nm the smaller cluster size the smaller ID/IG. A broad single band that we observed after annealing and absence of separated D- and G-bands can be an evidence of the presence of very small and highly disordered carbon clusters having dimension of 1 nm or less. Increasing Tan up to 850 °C leads to shift of the Raman band toward high frequency but the intensity of the band was not changed significantly. "Blue" shift can be explained most likely by some stress relaxation or increasing of the size of the carbon clusters. But even at highest annealing temperature the Raman band is still single.

The FTIR spectrum of the initial a-SiC film (Fig. 4, spectrum 1) is characterized by a wide absorption band with a maximum at 760 cm^{-1}, which is due to streching vibrations of Si-C bonds, and high-frequency shoulder at 1000 cm^{-1}, whose origin has not been unambiguously established by now. It is believed that it is caused by hydrogen trapped from the residual atmosphere. As the temperature of vacuum annealing increases, the high-frequency shoulder disappears. In this case, the basic absorption band narrows and shifts to high frequencies. The high frequencies shift and narrowing of the Si-C absorption band with temperature is a clear evidence of ordering of the interatomic bonds. A steep descent of the high frequency side of the absorption band after the annealing at 750 °C and above can be an indicator of the formation of a nanocrystalline phase. Thus, with an increase in the temperature of vacuum annealing, the following structure changes are observed in amorphous silicon carbide films: (1) dehydrogenation of the structure of a-SiC:H films and the formation of free carbon clusters at 750 °C and above, (2) ordering of interatomic bonds in a-SiC films.

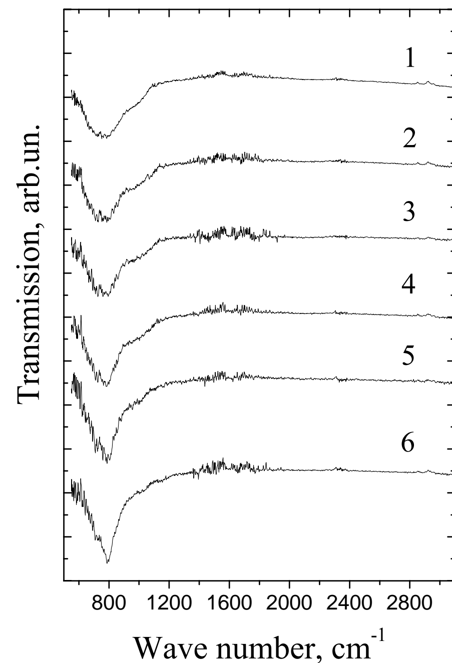

Fig. 4. IR transmission spectra of the a-SiC films: 1 – initial film at 20 °C; 2 – 450 °C; 3 – 550 °C; 4 – 650 °C; 5 – 750 °C; 6 – 850 °C.

We have compared the temperature dependences of the wettability of amorphous silicon carbide films with tin and that of some relative materials like graphite, glass carbon, polycrystalline diamond, monocrystalline silicon and silicon carbide (Table 1). It is seen that carbon materials, regardless of their crystal structure, are inactive with respect to tin over a wide temperature range and the degree of silicon wettability with tin is rather high and considerably increases with temperature. The contact angle for tin on crystalline silicon carbide is 140° and does not practically change up to 1150 °C [11].

A peculiar state of substances in the surface layer stems from the fact that the chemical bonds of the surface atoms are uncompensated. This gives rise to the excess energy of the surface atoms as compared to that of the atoms within the bulk material. A tendency to

Table 1

Wetting angles with tin for differenf types of materials.

Material	Temperature region,°C	Wetting angle, degree	Reference
Graphite	300 - 1000	148-140	[11]
Glass carbon	300 - 1000	140-132	[11]
Polycrystalline diamond	300 - 1000	130-124	[2]
SiC	400 - 1150	140	[8]
SiO_2	900	127	[12]
Si (111) Si (100)	900 900	44 35	[11]

minimize the surface energy manifests itself in the surface wettability. The wettability can be characterized by the value of contact angle, θ, that is a dihedral angle between the planes tangent to surfaces of a liquid and a solid at the point of contact. There is a correlation between the value of the contact angle and the intensity of the processes occurring at the solid-liquid-gas interface. A high contact angle $\theta > 90°$ points to a slight interaction between the liquid and the film, which is caused by physical forces (dispersion, dipole-dipole interactions, formation of the hydrogen bonds, etc.). A low contact angle ($\theta < 30°$) is due to the chemical interaction that proceeds at the interface.

To explain the absence of the difference in wettability of the initial films of hydrogenated and unhydrogenated amorphous silicon (see fig.1), one should suggest that the chemical states of the surface layers of these films are similar, in other words, hydrogen mainly is inside of the film. The common tendency for a decrease of the contact angle with increasing temperature points to an increase in the adhesion interaction of the metal with the film surfaces.

The step observed in the temperature dependences of the contact angles, θ(T), for the a-SiC:H films in the temperature range from 350 to 600 °C is anomalous. This is indicative of the formation of a peculiar surface layer, whose properties differ from those of the film material. Slight change and high values of the film contact angles in the above temperature range indicate that this layer cannot be formed by silicon atoms (see tabl. 1). A surface passivation in this temperature range with atomic hydrogen, which diffuses at high temperatures to the surface, hinders surface wettability of a-SiC:H films. Earlier we have established [1, 2] that hydrogenation of the surface of polycrustalline diamond films under the action of microwave plasma in a hydrogen atmosphere essentially increases of the contact angle for water on the film (up to θ=93°) as compared to oxidation (θ=32°). This was attributed to a decrease in the film surface energy due to the hydrogen adsorption induced surface reconstruction of the films toword forming of sp2-hybridized state of carbon, a decrease in the dipole moment of the surface and saturation of dangling bonds with hydrogen .

This allows to suggest that at temperatures above 300-350 °C there is a formation of a ultrathin layer of free carbon on surface of the a-SiC:H film. Clustering of free carbon is really observed in the bulk of a-SiC:H film at high annealing temperature (see fig. 3). So, we believe that stabilisation of the wetting angle for a-SiC:H film is related to the following reasons: (i) the passivation of the surface by hydrogen; (ii) a formation of a very thin layer of free carbon on the sample surface. Both reasons hinder the wetting of the surface. At the temperature above 650 °C , the bonds of hydrogen with silicon (Si-H), and carbon (C-H) atoms are break and hydrogen escape from the surface. As a result, the contact angle decrease rapidly. From the slope of the θ(T) curve at T>600 °C the a-SiC:H film surface, one can conclude that the peculiar surface layer has disappeared. It might be due to the desorption of the carbon surface layer due to oxidation with oxygen of the residual atmosphere at high temperatures.

For a-SiC film the effect of the wetting angle stabilisation in the range of 350-600 °C is weaker because of the low hydrogen content on the film surface, that exclude its passivation. The lower θ value to 140° at the temperature above 600 °C (note, that the same value is typical for crystalline SiC at 700 °C) might be attributable to interatomic bonds ordering with formation of nanocrystallites SiC.

Finally, we can summarize the presented results as following. Mechanism of the thermally stimulated change of the wettability of the a-SiC:H and a-SiC films by tin melt is connected with: (i) enrichment of the a-SiC:H film surface by hydrogen with subsequent dehydrogenation at high temperature (ii) clusterisation of free carbon at 650 °C and above with subsequent surface cleaning at high temperature; (iii) structure ordering of a-SiC.

Conclusions

The temperature dependence of the adhesion properties of the tin melt on the surfaces of films of hydrogenated and unhydrogenated amorphous silicon carbide has been studied. Based on analysis of wetting of amorphous silicon carbide films and related materials (graphite, glass carbon, diamond, silicon, silicon carbide) and the structural studies of the films after vacuum annealing, we have made a conclusion that the variation

of the tin contact angle of the a-SiC:H films after their thermal treatment is connected with the surface chemical state changes, which is attributed to the surface passivating with hydrogen, ultrathin carbon layer formation on the film surface and following surface cleaning at high temperature, whereas for a-SiC films these variation is attributed to structure ordering of a-SiC and formation of SiC nanocrystallites.

Acknowledgements
The autors wish to thank A. V. Semenov (Institute of Single Crystals of the National Academy of Sciences of Ukraine, Kharkov) for the supplying of a-SiC films for investigations.

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Вплив термічної обробки на адгезію розплава олова до поверхні плівок аморфного карбіду кремнію

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Проведено порівняльний аналіз впливу температури вакуумного відпалу плівок аморфного карбіду кремнію a-SiC та a-SiC:H на їх структуру та змочуваність розплавом олова. Плівки зі складом, близьким до стехіометрічного, були отримані двома методами: реактивним магнетронним розпиленням кремнію в атмосфері Ar-CH4 (a-SiC:H) та іоно-плазмовим осадженням з використанням модифікованого вакуумно-дугового джерела з карбіду кремнію (a-SiC). Капілярні властивості поверхні вивчали методом лежачої краплі в інтервалі температур від 250 до 7000С у вакуумі 1·10-3 Па. Аналіз структури плівок проводили з використанням Фур'є спектроскопії та спектроскопії комбінаційного розсіювання світла. Показано, что зміни змочуваності та підвищення адгезії рідкого олова до поверхні плівок внаслідок термовідпалу узгоджуються із змінами їх структури та хімічного стану поверхні. Для a-SiC плівок спостерігається упорядкування міжатомних зв'язків та утворення нанокристалітів карбіду кремнію. Для a-SiC:H плівок спостерігається видалення водню, який пасивує поверхню, кластеризація вільного аморфного вуглецю, та видалення його з поверхні при підвищенні температури.