Fluorination of silicon carbide thin films using pure F₂ gas or XeF₂

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Abstract

Two fluorination methods: direct fluorination using F₂ gas and fluorination by the decomposition of fluorinating agent XeF₂ have been applied to silicon carbide SiC thin films in order to form a composite of carbide derived carbon film together with residual silicon carbide. Before and after fluorination, the thin films have been characterized by Scanning Electron Microscopy, Rutherford Backscattering spectroscopy, Fourier Transformed InfraRed and Raman spectroscopies. Whereas direct fluorination leads to irreversible damages into the thin films, XeF₂ method allows a progressive etching of the silicon atoms and the formation of non-fluorinated carbon.

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1. Introduction

Due to high hardness, low friction coefficient, good chemical inertness and good biocompatibility, the amorphous carbon coatings are of great interests for numerous tribological applications. However, their tribological properties are very sensitive to the environment factors [1,2] and depend on the deposition method and conditions. To increase their tribological performances in aqueous conditions, the presence of silicon atoms can be useful [3]. Plasma-Assisted Chemical Vapour Deposition allows to obtain a multilayer structured coating with alternating layers of silicon-doped a-Si₁₋ₓCₓ:H and undoped a-C:H layers. Another way to produce carbon-SiC thin films consists in the extraction of silicon atoms from carbide by chlorination process [4,5]. Gaseous chlorine is known to react with metallic atoms at high temperature (600 – 900 °C) to form most of the time a gaseous chloride which is easily removed, and a carbon called carbide derived carbon (CDC). Carbon nature depends on parameters such as crystallographic structure of the carbide precursor, steric hindrance of the chloride or chlorination conditions [5,6].

Many studies have been devoted to the chlorination of silicon carbide because of the multiplicity of carbon structures found after chlorination : from amorphous carbon to carbon onions and nanodiamonds [7]. However, in order to thermodynamically favor the formation of SiCl₄ instead of CCl₄, a chlorination temperature of about 900 °C is required [4]. In order to decrease the synthesis temperature, fluorination can be chosen as another way of halogenation [8]. In the same way than chlorination, fluorination of silicon carbide can results in a gaseous silicon fluoride which should be easily extracted from the carbon structure. However, thermodynamic calculations are needed in order to optimize the synthesis temperature and the carbide/fluorine ratio. In particular, formation of fluorinated carbons must be avoided. Fluorination is not an easy chemical synthesis route and can be conducted by different ways: by electrochemical reaction using a liquid fluorinating agent such as HF [9], by volatile inorganic fluorides in glow discharge using for example a CF₄-plasma [10] or by the reaction of gaseous atomic or molecular fluorine [11–13]. On one hand, electrochemical fluorination needs a very high concentration of HF, i.e. a very corrosive media, to obtain not a very high reaction yield [14], on the other hand, plasma fluorination is efficient for surface functionalization but not for an homogeneous fluorination of the material bulk. So, for the bulk reaction such as the transformation of carbide into carbon, gaseous fluorination should be the best way to proceed. Two types of fluorine species can be used: molecular fluorine delivered from 1 atm. pressure of pure fluorine gas or atomic fluorine generated by the decomposition of a fluorinating agent. Amongst the fluorinating agents one is particularly interesting namely XeF₂. This compound which is a solid at room temperature has a vapor pressure of 3.8 mm Hg at 25 °C and of 318 mm Hg at 100 °C [15]. So rather low increase of the temperature leads to its sublimation and the gaseous form can easily decompose into inert gaseous xenon and atomic fluorine [15]. The advantage of XeF₂ is that its thermal decomposition can be put under control to release a definite quantity of reactive fluorine during the reaction and thus to control both the reactivity with fluorine and the fluorine level.

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In this work, the main attention was paid to comparison of treatment of silicon carbide thin film by 1 atm. molecular fluorine gas (process called direct fluorination) and by XeF₂ (process called controlled fluorination). Investigation of the thin film morphology should allow a better comprehension of the fluorination mechanism and more particularly kinetic effects not predicted by thermodynamical calculations. For this aim, Rutherford Back Scattering spectroscopy (RBS) combined with Scanning Electron Microscopy (SEM), Infrared and Raman spectroscopies have been used and correlated.

2. Experimental Methods

2.1. Synthesis

Silicon carbide thin films were deposited by reactive magnetron sputtering at 13.56 MHz frequency in an Alcatel SCM 450 sputtering equipment under different Ar-N₂ gas atmospheres from a silicon carbide target [16]. SiC thin films were deposited on glassy carbon for RBS and fluorination purposes. The films composition has been confirmed by RBS. Its thickness determined both by sputtering rate and by SEM, was around 300 nm.

Two fluorination ways were used: fluorination under 1 atm. of pure fluorine gas stream (Fig. 1a) and fluorination by the decomposition of XeF₂ as fluorinating agent in a closed reactor (Fig. 1b). For direct fluorination, gaseous fluorine was purchased from Solvay Fluor (purity 98-99% V/V with HF max. 0.5% V/V and other gases, primarily O₂/N₂ at approximately 0.5% V/V). Fluorine flow was set at 8 mL.min⁻¹ i.e. fluorination conditions close to those established in a closed reactor. Prior to and after fluorination, the thin film was outgassed at 130 °C under nitrogen gas for 2 hours except the samples fluorinated at temperature lower than 130 °C for which no outgassing was performed before fluorination. The first outgassing is made in order to remove traces of moisture, which could form HF in the presence of fluorine gas. As a matter of fact, HF can catalyse the fluorination but this process is not controlled because the moisture content is not stable.

For fluorination by XeF₂, a closed reactor was used in order to preserve the defined fluorine amount released by the thermal decomposition of XeF₂. It was assembled under argon atmosphere in a glove box. Because of the low decomposition temperature of XeF₂, solid XeF₂ and carbide have been placed in the reactor under argon atmosphere. The equilibrium XeF₂(s) ↔ XeF₂(g) occurs and XeF₂ decomposes into gaseous xenon and atomic fluorine on the surface of the target [17]. Fluorination conditions (120 °C) have been chosen in order to favour the kinetic of XeF₂(g) decomposition, so both fluorination temperature and pressure are nearly the same for the two different fluorination ways. But, concentrations of the reactive species F₂ and F⁻ change. The corresponding reactions are the following:

\[ \text{XeF}_2 \rightarrow \text{Xe} + 2\text{F} \]  \hspace{1cm} (1)

\[ \text{SiC} + 4\text{F} \rightarrow \text{C} + 2\text{SiF}_4 \]  \hspace{1cm} (2)

2.2. Physico-chemical characterizations

Thermodynamic calculations of the reaction products in the system SiC/flourine-containing gases have been conducted over 25-1000 °C temperature range with 50 °C step using a Gibbs energy minimization software. The program Factsage 5.3 (GTT technologies, Germany) was used. The effects of temperature and pressure on the composition of equilibrium reaction products have been studied. The hypotheses necessary to carry out the thermodynamic calculations concern the choice of the gas and solid phases and the choice of thermodynamic data. The calculations were done for a closed system with a constant total pressure and ideal gases (activity coefficients are equal to unity). However, whereas thermodynamical data on gaseous fluorine carbon compounds are referenced, a lack in thermodynamic data on solid carbon fluorides must be noticed. Such lack could easily be offset by knowledge acquired since 20 years in our laboratory on carbon fluorides preparation [18].

The film composition was investigated by RBS using 2 MeV alpha particles and 15 nA current intensity. A charge of 10 μC was collected at 165° detection angle. As amorphous carbon substrate was used, its RBS signal appears at lower energy than the film constituent ones and does not overlap. To determine the composition, experimental spectra were simulated using the SIMNRA software [19].

A JOIN YVON T64000 spectrometer with a charge-coupled device multichannel detector was used for Raman investigations at room temperature. The radiation source was a 514.5 nm argon laser line. The laser power was tuned to low power (100 mW) in order to avoid the sample decomposition under the beam. 3 scans of 640 s were made for a single spectrum. The resolution was equal to 0.08 cm⁻¹.

Fourier Transformed Infrared FTIR spectra were measured over the range 4000-400 cm⁻¹ by a FTIR Nicolet 5700 spectrometer equipped with a diffuse reflection accessory. The resolution was equal to 8 cm⁻¹. For a single spectrum, 512 scans were made on the overall range.

Fig. 1. a) fluorination under pure fluorine gas, b) fluorination under decomposition of XeF₂.
SEM micrographs were recorded by Cambridge Scan 360 SEM operating at 1 kV.

3. Results and Discussion

3.1. Thermodynamic Aspect

For thermodynamic simulations made for the SiC/Cl2 system [4], the thermodynamic probability of the carbon formation increases with the reaction temperature. If one mole of silicon carbide reacts with more than two moles of chlorine, a temperature as high as 900 °C is required in order to form carbon and to avoid CCl4 formation.

According to our thermodynamic simulations for the SiC/F2 system (Fig. 2), carbon can be formed at room temperature if fluorination is applied. So the use of fluorination instead of chlorination should favor a significant decrease of the reaction temperature. The SiC/F2 ratio of 1/2 should be favored in order to obtain the highest quantity of carbon. For higher quantity of fluorine, some gaseous carbon fluorides are formed but they do not pollute the carbon formed.

3.2. Fluorination conditions and thin film composition

In order to ensure total conversion of silicon carbide into carbon, excess of fluorine gas has been inserted in the furnace whatever the fluorination F2 or XeF2. Indeed, thermodynamic simulation does not take into account the kinetic limitations which reduce the corrosion rates of carbide at temperatures below 400 °C. Higher excess of fluorine has been used for direct fluorination because the system is not closed and not the overall gaseous fluorine flux is efficient for carbide fluorination. Thus, the calculated equilibrium composition was not always reached under the experimental conditions.

In agreement with thermodynamic calculations, low fluorination temperatures have been used to form carbon from carbide and also to avoid carbon fluoridation. Indeed, non crystallized carbons react with fluorine to form carbon fluorides even at room temperature [13].

Whatever the fluorination conditions under fluorine gas (Table 1), silicon is etched from the silicon carbide in order to form silicon tetrafluoride SiF4. The level of resulting carbon can be correlated with the reaction temperature (Table 2). The lower the temperature, the higher the amount of the physisorbed species such as SiF4, F2, CF4, C2F6 trapped in the porous carbon matrix. The fluorine level is high for all the samples. One part is involved in nickel difluoride NiF2 which comes from the decomposition of the inner passivating layer of the reactor. For low synthesis temperature (the sample is then denoted SiC-F2-3), the F/C ratio is about 2 whereas for higher temperature, this ratio is lower than 1. For low temperature, fluorine could be either trapped at the molecular state by the amorphous porous carbon or bonded on carbon dangling bonds. CF2 and CF3 groups could also be formed. With temperature increase, fluorine gas can either be outgassed from the amorphous carbon or react with carbon to form strong covalent carbon-fluorine bonds [13].

For fluorination using XeF2 decomposition, a SiC/F2 molar ratio of 1/20 is too low to totally extract all the silicon atoms from the carbide. But this result shows that, thanks to this fluorination method, partial etching is possible and can result in a SiC/CDC composite. For higher molar ratio, silicon is totally etched and higher carbon level is obtained for longer fluorination time because of physisorbed fluorine gas outgassing. In order to deliberate between physisorption or chemisorption of fluorine, Infrared spectroscopy measurements have been performed.

3.3. Carbon-fluorine interaction

Fig. 3 shows FTIR spectra of SiC before and after fluorination by F2 or by XeF2. Because of the refexion diffuse mode used for FTIR analysis, first signal/noise ratio is low and no skeletal vibrations of SiC at 820 cm\(^{-1}\) and 900 cm\(^{-1}\) can be observed [20,21] whereas they can already been observed by transmission mode for SiC thin film before fluorination [16]. Indeed, no information can be obtained from SiC by such a mode, only information on carbon-carbon or carbon-fluorine vibrations could be hoped. After direct fluorination, 3 main absorptions bands appear at 1180, 1450 and 1620 cm\(^{-1}\). The first one is attributed to covalent carbon fluorine bonds such as in covalent graphite fluorides [12]. The two others are related to the formation of carbon i. e. sp2 C-C and C=C, respectively [22].

Spectra of samples fluorinated by XeF2 indicate that only carbon vibrations appear. No carbon-fluorine bonds are formed contrary to fluorination with fluorine gas although the synthesis temperatures are approximately the same. This can be explained by either the different reactive species involved in the two fluorination methods or the higher over-stoichiometry of fluorine used for direct fluorination. This last argument must be moderated by the fact that even if the fluorine amount is higher for the case of direct fluorination, the gas-solid contact time is short and the furnace volume is higher than that of the XeF2 closed reactor (260 mL and 100 mL, respectively). So, the fluorination of the carbon was not observed. Fluorine F reacts only with silicon atoms to form SiF4.

3.4. Morphological evolution with fluorination

Whatever the fluorination method, SEM images (Fig. 4) indicate a similar fluorination mechanism. Silicon atoms are extracted from the

<table>
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<tr>
<th>Table 1</th>
<th>Fluorination conditions.</th>
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<tr>
<td></td>
<td>Fluorination temperature (°C)</td>
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<tr>
<td>SiC-F2-1</td>
<td>130</td>
</tr>
<tr>
<td>SiC-F2-2</td>
<td>130</td>
</tr>
<tr>
<td>SiC-F2-3</td>
<td>30</td>
</tr>
<tr>
<td>SiC-XeF2-1</td>
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<tr>
<th>Table 2</th>
<th>Thin films composition determined by RBS (at. %).</th>
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<tr>
<td></td>
<td>Si</td>
</tr>
<tr>
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</tr>
<tr>
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<tr>
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</tr>
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<td>SiC-XeF2-3</td>
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amorphous silicon carbide matrix which has a columnar-like structure. This results in a formation of a new thin film where carbonaceous columns represent a matrix surrounded with porous columns (Fig. 4e, f). The porous columns are about 20 nm in diameter and allows the diffusion of both fluorine and silicon fluoride formed during the reaction. The high reactivity and excess of molecular fluorine used for direct fluorination lead to a reorganization of the porous structure (Fig. 4d) which destroys the carbonaceous matrix and provokes some wrenches and folds in the thin films (Fig. 4b). By treatment with XeF₂, the reorganisation of the porous structure is avoided and CDC thin film surface is homogeneous.

3.5. Carbon structure

Representative Raman spectra of the films after fluorination are shown in Fig. 5. It must be noticed first that for untreated SiC thin films the typical strong Raman bands at about 790 and 970 cm⁻¹, assigned to transversal and longitudinal optical phonons, respectively, whatever the polytype of SiC [23,24], do not appear because of the amorphous character of the studied thin films [16]. After fluorination, two typical bands of carbon appear. The broad band at 1600 cm⁻¹ is typical either for amorphous non-hydrogenated carbon [25] or for carbon in diamond-like carbon films and is attributed to bridged graphite [26]. A second band at about 1350 cm⁻¹ is related to the breathing of six carbon rings of graphite. Its intensity appears as a good parameter to estimate the order degree in disorganised carbon [27].

Several spectra have been registered from the border to the center of the thin films for SiC-F₂-1 (Fig. 5b) and such evolution is representative for all the samples whatever the fluorination conditions. One can observe that the full half width of carbon bands is larger when the recording is performed near the border because of a more disordered character of the carbon. Such an effect is due to the fluorine reactivity in 2 steps: etching of silicon atoms and carbon formation are followed by formation of carbon-fluoride. This latter process occurs when the fluorine level is not controlled during the synthesis in the same way as the case of direct fluorination. Raman data are summarized in the Table 3 where average values are obtained.

Fig. 3. FT-IR spectra of SiC after fluorination by F₂ or by XeF₂ (Highlighted bands are related to C-F bond vibrations domains).

Fig. 4. SEM images of a) SiC carbide before fluorination, b,d,f) after fluorination under F₂, c,e) after fluorination under decomposition of XeF₂.
from 3 spectra recorded on the center of the thin films i.e. where fluorination is less effective.

So the presence of carbon even for the slower fluorination kinetics is proved by this characterization. Robertson and Ferrari have suggested a classification of the carbon type owing to the position and the shape of the carbon bands [28]. Such classification is particularly judicious for amorphous carbon thin films. In this method, the fitting of carbon bands requires an asymmetrical Breit-Wigner-Fano function (BWF) [29] for the G band and a Lorentzian for the D band. Fig. 5c) shows application of this method to a typical Raman spectrum of the studied samples.

Calculated on the basis of fitting, \( \frac{I_D}{I_G} \) ratio corresponds to the ratio of the area of the D band over the one of the G band. Then coherence length \( L_c \) in the graphitic plane can be deduced owing to the relation: \( L_c = 0.740 \left( \frac{I_D}{I_G} \right)^{1/2} \). Owing to the Table 3 and because 0% carbon sp\(^3\) is not possible, the thin films can be put at the beginning of the step two of Ferrari and Robertson classification (Fig. 5a). It means that carbon atoms in the thin films exhibit mainly the sp\(^2\) carbon hybridization and some graphitic nanocrystallites are expected with coherence length ranged in between 6 to 8 agglomerated aromatic rings. At the Raman scale, no differences are registered according to the fluorination method.

4. Conclusion

Unusual thin films with bimodal dispersion of layers, i.e. both SiC and CDC-SiC, have been prepared by an original fluorination method using XeF\(_2\) decomposition. Atomic fluorine formed by the decomposition of gaseous XeF\(_2\) on the target surface reacts preferentially with silicon atoms and is evolved to the gas phase. Such a way allows the fluorination to be controlled contrary to the direct process using molecular fluorine. Moreover, the release of SiF\(_4\) allows a progressive cleaning of the thin films surface and this species is easily removed from the surface. The formed carbons rearrange themselves to form a real nanostructured carbon film, which is composed of graphite nanocrystallites. So, fluorination can be used for the synthesis of carbon films on carbide surfaces at lower temperatures than for the case of chlorination. It can also be used for the modification of the surface properties of other thin films or industrial materials for potential technological rewards [30]. For example, the unique microstructure of CDC obtained by fluorination method on carbide thin films could be very attractive for tribological properties.

Tribological measurements are under progress.

References