SiCN coatings prepared by PACVD from TMS-NH3-Ar system on steel
M. Ducarroir, W. Zhang, R. Berjoan

To cite this version:
M. Ducarroir, W. Zhang, R. Berjoan. SiCN coatings prepared by PACVD from TMS-NH3-Ar system on steel. Journal de Physique IV Colloque, 1993, 03 (C3), pp.C3-247-C3-254. <10.1051/jp4:1993333>. <jpa-00251390>

HAL Id: jpa-00251390
https://hal.archives-ouvertes.fr/jpa-00251390
Submitted on 1 Jan 1993

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
SiCN coatings prepared by PACVD from TMS-NH₃-Ar system on steel

M. DUCARROIR, W. ZHANG(1) and R. BERJOAN*

IMP-CNRS, Université de Perpignan, 52 Avenue de Villeneuve, 66860 Perpignan cedex, France
* IMP-CNRS, BP. 5, Odeillo, 66125 Font Romeu cedex, France

Abstract

SiCN coatings with continuous composition between Si₃N₄ and SiC (rich in Si) have been prepared by acting on the tetramethylsilane (TMS)/ammonia ratio in the gas phase. The deposit compositions (10µm thick films) have been investigated by different means which stress the difficulties encountered. Nevertheless the trends are in fair agreement. An increase in ammonia partial pressure favors the incorporation of N in the deposits. XPS studies of the samples lead to the conclusion that the chemical environments of Si, C, N are more complicated than in a mixture situation; there would be various bonding states. Deposition rates range from 12µm h⁻¹ up to 30µm h⁻¹ and are largely increased when dilution is reduced. Hardness and Young's modulus are driven by the C/N ratio: Hᵥ lies between 22.6 GPa (Si₃N₄) to 26.2 GPa (SiC) with respectively apparent Young's modulus from 250-295 up to 357-431. All the films exhibit an adhesion of same order though N tends to increase the critical loads.

Introduction

The resistance of silicon carbide and silicon nitride to high temperatures and corrosive chemical atmospheres as well as other excellent properties make them attractive materials for a large field of applications. Although SiCN deposits were previously obtained at elevated temperatures (1-4), few experiments have been carried out at low temperature and furthermore on steel substrate. Some data may be found in literature for experiments carried out with gaseous mixtures SiH₄+CH₄ or SiH₄ + C₂H₄(CH₄) + NH₃ (5-7). Besides PACVD, amorphous SiₓCᵧNy:H films were prepared by rf. reactive sputtering (8). In the laboratory, the technique of depositing silicon carbide coatings on steel has been well developed(9-10). The preparation of silicon carbide coatings on steel substrate (4135 steel) was performed in a cold-wall vertical tubular PACVD reactor using tetramethylsilane - argon gas system. Deposits of silicon carbide with various Si:C atomic ratios were obtained. The optimized deposition conditions giving the best mechanical properties(e.g. microhardness and critical load in scratch testing) of Si-C coating on steel were found (10).

CVD Silicon nitride has been extensively used for passivation and surface protection purposes and is well accepted because of its physical and chemical stabilities. In order to combine the excellent characteristics of silicon carbide and silicon nitride, attention has been drawn on the development of multi-component silicon, carbon and nitrogen-based materials. The objective of the present work has been to investigate the influence of nitrogen addition to the Si-C coating properties.

(1) Present address: Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980, Japan

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jp4:1993333
Experimental Procedures


Briefly, the deposition was performed in a cold-wall PACVD reactor. The plasma reactor consists of a vertical silica tube (28 mm in diameter and 300 mm long) with an external copper coil coupled to an RF generator (2 MHz). Coatings were deposited on polished (diamond paste 1 micron) grounded substrates. The substrate (4135 type steel) of 16 mm in diameter and 5 mm thick was fixed on the substrate holder (perpendicular to the gas flow) by screws. The heads of the screws obscured a small area of the substrate surface and thus provided a convenient area for comparison between the coated and uncoated surface. In this device, the plasma generation and the substrate heating are matched. So for a given input power, temperature is adjusted by acting on the distance of the substrate to the coil and kept constant (873 K) for all the experiments carried out.

The gas mixture (TMS, NH₃ and Ar) flows from the bottom upward in order to minimize thermal buoyancies, and each flow rate is regulated by mass flow controllers. The total pressure is adjusted by means of a throttle valve just before the mechanical pump and is measured with an absolute pressure gauge. The reactant purities are: 99.9% for TMS (Aldrich-Chemie) and ammonia (Air Liquide), and 99.99% for argon (Air Liquide), respectively. No further purification is used. After pumping down the reactor, a pure argon plasma is then established at the selected temperature to clean the substrate by in situ sputtering.

2. Coating properties.

In various previous papers PECVD film containing Si:C:N were reported. Typically at low temperature they are said to be amorphous with trapped H and N. Composition and structure of the films are not always clearly detailed.

Different analytical techniques have been used to identify the obtained coatings (usually 5 to 10 μm thick, and some ones in the range of 10-18 μm).

The atomic composition of SiCN coatings was determined by a CAMEBAX electron probe microanalyser (EPMA) using β-SiC, Si₃N₄, SiO₂, and Fe as standards. All the measurements were carried out at 15 kV acceleration voltage and 150 nA sample current. As charge effect on the insulating surface during EPMA occurs it could hinder the precise determination of SiCN samples, especially the Si₃N₄-like coatings. 

Rutherford backscattering (RBS) technique was also employed for the determination of some coating compositions. This analysis was performed with a He⁺ ion beam of an energy of 2 MeV.

XPS and XAES analyses were performed using a RIBER CAMECA SIA 200 system, at a base pressure of about 10⁻⁹ torr (mbar). The AlKα-line at 1486.6 eV was used to ionize the elements present in the samples. XPS and XAES spectra were recorded in the energy range between 900-1650 eV, allowing to obtain the C₁s, N₁s, O₁s, Si₂p and Si₂s photoelectron peaks. All spectra were recorded after 30 minutes Ar⁺ sputtering: 4 keV-4μA/cm². The Si KLL Auger transitions were also excited by the Bremsstrahlung radiation associated with the AlKα-line. These last Auger transitions were obtained with a low intensity, because the AlKα-line was monochromatized by passing through an Al window.

The energy resolution was fixed at 1 eV for all the spectra and counts were collected at interval of .25 eV. Quantitative analysis was performed by means of elemental sensitivity factors (Si = 0.24, N = 0.42, O = 1, C = 0.25) which are slightly modified (mainly for O) in comparison to sensitivity factors reported elsewhere (11).

Indeed two reference silicon nitride compounds were analyzed first: the first one was a thin film (2060 Å) on silicon wafer, the second one a thick deposit (600μm) prepared at high temperature (1500 K). Application of these sensitivity factors allowed to obtain 1.35 < N/Si < 1.37. These values are reliable since a small amount of oxygen was also detected (figure 1). For these references, the line spectra are identical in regards to peak positions; therefore, the surface charging effect must be similar. The low intensity O₁s, C₁s lines may be attributed to redeposition in function of time. As a matter of fact they do not appear just after sputtering the sample surface. Figure (1) corresponds to accumulation of data from 4 scans (i.e. one hour), to improve the ratio signal to noise. It is interesting to note that full width at half maximum (F.W.H.M) for N₁s and Si₂p are respectively 2.2 ± 0.1 eV and 2.4 ± 0.1 eV.

These values suggest charge problems. As a result of the dielectric properties of the films, charge shiftings were observed. Therefore, it is very difficult to discuss chemical bonding through chemical shift measurements. Calibrations of the spectra by means of the peak position for adventitious carbon was not possible, as the samples contain carbon.
Nevertheless, some chemical informations have been obtained by measuring either the Auger parameter in regards to silicon; i.e. the difference between the Si KLL and the Si$_{2p}$ photoelectron peak energies $\alpha = E_k(\text{Si KLL}) - E_k(\text{Si}_{2p})$ or the modified Auger parameter $\alpha': \alpha' = \alpha + h\nu(\text{AlK}\alpha)$. Chemical information deduced from the examination of Auger or photoelectron line broadenings is doubtfull since peak enlargments may arise from variations in static charges.

The hardness of SiCN coatings were determined with a Shimadzu tester taking care that the indentation depth remains several times smaller than the thickness so that the subsurface deformation beneath the indenter is not influenced by the proximity of interfaces or free surfaces.

From a continuous microindentator (depth versus load), the apparent Young modulus $E/(1-\nu^2)$ of the films were calculated from the slope of the unloading curve at the maximum applied load (150mN).

Scratch adhesion testing was performed using a commercial scratch tester (supplied by CSEM, Switzerland) equipped with a Rockwell C diamond stylus (cone apex angle 120°, tip radius 0.2 mm). The tester is fitted with acoustic emission monitoring equipment which can detect emission in the vicinity of 100 kHz, in order to determine failure without the need for any microscopical observation. However, scratches were examined by optical microscopy and scanning electron microscopy (SEM) and the formation of features within the tracks correlated with the acoustic emission observations to investigate the reliability of using this technique to detect failure at the coating/substrate interface. In order to assess the relevance of the test for adhesion measurements all the scratches were examined optically and the load at which there were uncovered substrate visible regularly along the scratch track (by whatever failure mode this was achieved) was used to define the critical load ($L_c$).

### Results and discussion

1. Composition.

Figure 2 shows the dependance of the atomic concentrations of Si, C, N on the input gas composition represented by the TMS ratio $f = \text{TMS}/(\text{TMS+NH}_3)$. Whatever, the analytical method (EPMA full lines, XPS doted lines and X dots, RBS R dots, nuclear reaction r dots) the trend is similar. Lowering the C/N at. ratio in the gas (i.e decreasing $f$) induces a decrease of the C/N at. ratio in the film. The carbon content decreases while the nitrogen content increases. In other words, a nitrogen excess in the gas (ninefold) is necessary to form quite pure silicon nitride. The oxygen content in the bulk of the SiCN coatings was always less than 2 at.% The dots on the composition scale are relative to the Si$_3$N$_4$ reference previously mentionned. In front of large discrepancies and deviations to the global atomic balance encountered by EPMA mainly on the containing nitrogen sample surface, it is considered that this method must be regarded with care. Light metallisation does not improve the results. Furthermore, one can note that at the small value of $f(\leq 0.1)$ the N/Si atomic ratio in the SiCN is higher than 1.33 of the stoichiometry. Such phenomenon was previously mentionned in coatings prepared by different ways.
Ingo et al. (12) have detected the formation of N-N bonds by XPS analysis in silicon nitride deposited by dual ion beam sputtering: N-rich nitrides could also consist of stoichiometric material Si$_3$N$_4$ with nitrogen atoms embedded in the matrix. It could be also considered that the samples are not homogeneous at the scale of the analysis and that the high N/Si ratio may be a consequence of differences in the emission volumes of characteristic X-rays for the elements. For further discussion we have selected the XPS method which must lead theoretically to chemical bond informations. Table 1 summarizes the quantitative analysis results for the different samples, lists the modified Auger parameters ($\alpha'$) and the full width at half maximum (F.W.H.M) measured for the different peaks. $\alpha'$ depends on the chemical environment. For $f = 0$, in comparison with recently published values (13), $\alpha'$ is characteristic of the silicon environment in Si$_3$N$_4$. When $f = 1$, $\alpha'$ higher than $\alpha'_{Si}$ may be attributed to a small contribution of Si-Si bonds associated with Si-C bonds; this is in agreement with the Si/C ratio. For $0.1 \leq f \leq 0.75$ intermediate $\alpha'$ values should be assigned to the presence of different bondings: both Si-C and Si-N or Si-C-N.

Table 1: Analytical data of coatings: XPS measurements

<table>
<thead>
<tr>
<th>f</th>
<th>C/N gas %</th>
<th>$\alpha'$ (eV)</th>
<th>Experimental F.W.H.M (eV)</th>
<th>at % Si</th>
<th>C</th>
<th>N</th>
<th>at balance mixture SiC Si$_3$N$_4$ Si</th>
<th>Calculated F.W.H.M S$_{12p}$</th>
<th>Calculated shift.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>ref.</td>
<td>-</td>
<td>-</td>
<td>43</td>
<td>0</td>
<td>60</td>
<td>- - 15 2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.05</td>
<td>0.21</td>
<td>1714.5</td>
<td>2.2 4.6 2.6</td>
<td>40</td>
<td>7</td>
<td>50</td>
<td>2.5 4.5 12.5 -</td>
<td>2.563 0.85</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.44</td>
<td>1714.1</td>
<td>2.9 4.8 2.7</td>
<td>41</td>
<td>12</td>
<td>48</td>
<td>5 7 12 29</td>
<td>2.591 0.53</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>1.33</td>
<td>1714.6</td>
<td>2.7 3.8 2.8</td>
<td>43</td>
<td>28</td>
<td>28</td>
<td>22.5 5.5 7</td>
<td>2.202 0.08</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>4</td>
<td>1715.2</td>
<td>2.6 2.6 2.8</td>
<td>47</td>
<td>37</td>
<td>15</td>
<td>357 1.25 3.75</td>
<td>2.071 &lt;</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>12</td>
<td>1715.4</td>
<td>2.4 3.2 2.7</td>
<td>45</td>
<td>38</td>
<td>10</td>
<td>37.5 1.5 2.5</td>
<td>2.041 &lt;</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>1715.5</td>
<td>- 2.3 2</td>
<td>55</td>
<td>47</td>
<td>0</td>
<td>47</td>
<td>8</td>
<td>-</td>
</tr>
</tbody>
</table>

In regards to Borsella's data (13), the $\alpha'$ value for $f = 1$ agrees with a film in which a small number of Si-Si bonds are present. On table 1, it should be noticed the strong broadening of the N$_{1s}$ and C$_{1s}$ core level peaks. For the former, this could be assigned to nitrogen bonded to carbon, whose occurrence goes through a maximum in the range $f = 0.1$, 0.25. C$_{1s}$ peaks are correletively larger, but the interpretation is more complex due to the various bondings in which carbon may be present: C=O as contaminant, C-Si, C-H, C-C as in graphite or diamond (14). Therefore, in front of this complexity the peak fitting must be considered with care. Nevertheless we did it.

Referring to Si$_{2p}$ peak, it is impossible to relate the broadening with the presence of mixed bondings in the film. This is supported by the results of the mathematical convolution of two Gaussian curves separated by 1 eV (i.e. experimental shift between Si$_{2p}$ in SiC and Si$_3$N$_4$) for contents corresponding to the ratio SiC/Si$_3$N$_4$. For cases $f = 0.05,0.1$, an homogeneous mixture of phases could be responsible for the Si$_{2p}$ F.W.H.M as calculations are in agreement with measurements (see table 1). In other cases, a mixture should lead to narrower peaks and the peak broadening could arise from static charges due to an heterogeneous surface with more or less insulating regions (15).
Furthermore, the valence band spectra for the films obtained with $f = 0.25$, $f = 0.1$ (large amounts of NH$_3$) were examined. In regards to the results of Hicks (16), the spectra do not reveal the features suggesting the presence of H bonded either with Si and/or C. So, we have no problems of shift due to incorporation of H as it was mentioned by Katayama (17).

The changes in $\alpha'$ values with the variations of the sample compositions can be attributed unambiguously to silicon bondings variations. If the $\alpha'$ evolution could agree with a Si$_3$N$_4$-SiC mixture in which relative proportions change from SiC + Si to Si$_3$N$_4$ containing a little amount of carbon, however the important C$_{1s}$ and N$_{1s}$ broadenings suggest that the bonds distribution is more complicated than the bonds distribution in a mixture either binary or ternary. As illustration, figure 3 shows a magnification of the C$_{1s}$ and N$_{1s}$ lines for $f = 0.05$. The experimental N$_{1s}$ and C$_{1s}$ lines as well as peaks fittings by two and three Gaussian components are respectively drawn. F.M.W.H of each component were fixed at $2.2 \pm 0.1$ eV as they are the full widths at half maximum obtained for the SiC + Si deposit and the Si$_3$N$_4$ reference samples. In this case, the deposit contains various kinds of chemical environments for carbon and nitrogen. The three C$_{1s}$ components can be attributed to:

- C in SiC configuration at $E_C = 1196.3$ eV.
- "free" carbon, (carbon not bonded to Si or N) at $E_C = 1194.7$ eV. This "free" carbon contains probably a part of residual contamination carbon.
- and probably C bounded to nitrogen (C-N bonds) at 1192.6 eV.

The two N$_{1s}$ components at 1081.5 eV and 1080 eV indicate the probable presence of respectively Si-N bonds and C-N bonds.

2. Deposition rate and deposit features

The deposits with various compositions have a compact appearance, free of gross porosity as shown in figure 4. There is no large columnar growth towards the top surface of the coating, perhaps indicating continuous nucleation of the material during deposition and an homogeneous growth.

Figure 3: Line shapes and peaks fittings for (left) N1s and (right) C1s in the sample $f = 0.05$.

Figure 4: Fracture scanning electron micrograph: deposit on steel obtained for $f = 0.05$. 
Therefore, the surface of the coating (less than 6 μm thick) is smooth and no obvious structural features can be observed on coating except of some circular caps which are perhaps the proof of hemispherical nucleation (18). The color of SiCN coatings becomes clear yellow when enough nitrogen is present. Otherwise \((0 < f < 1)\) the coatings appeared as grey silvered. By classical X-ray diffraction no peaks are observed. Only for \(f = 1\) a very large one is detected. Samples may be said amorphous or with very finely crystallite sizes. The film deposition rate was found to depend strongly on the TMS volume fraction \((f)\). Figure 5 shows the deposition rate at Ar concentration of 90% and 80% respectively.

![Figure 5](image_url)

**Figure 5**: Deposition rate of SiCN coatings as a function of ratio for two Ar concentrations.

For both series, the main trend is quite similar: an increasing as the ratio increases, especially at lower and higher \(f\) values \((0 < f < 0.2\) and \(0.75 < f < 1)\). It is to note that as the total gas flow is held constant, increasing \(f\) corresponds to the same change in TMS flow, while NH₃ decreases. In spite of the lower deposit thickness for the lowest value of \(f\) (large excess of NH₃), the efficiency in regards to silicon (ratio of silicon in deposit on input silicon) is higher than for \(f = 1\). Expressing simply the efficiencies lead to the following expression

\[
\eta_{\text{Si}}(\text{SiC}) = \frac{3f_{\text{SiC}}}{f_{\text{Si}}N_{4}} \cdot \frac{\rho_{\text{SiC}}}{\rho_{\text{Si}}N_{4}} \cdot \frac{M_{\text{SiC}}}{M_{\text{Si}}N_{4}} \cdot \frac{e_{\text{SiC}}}{e_{\text{Si}}N} \#
\]

with \(\eta_{\text{Si}}(\text{SiC}) = 1/100\). So, NH₃ increases the transformation rate of TMS. Any attempt of discussing the process on the basis of only these results is prevented by the complex nature of gaseous species and the process variations induced by \(f\) (residence time, mean free path, gas temperature). It should be noticed that NH₃, in the present case, does not inhibit the growth as it was established in previous conditions. When the concentration of input gases increases, the deposition rate increases probably as a consequence of active species fluxes and/or their concentrations.

3. Approach of coating properties

As commonly observed, the critical loads \((L_c)\) were found to increase linearly with increasing thickness in agreement with the predictions using critical shear stress (19). Furthermore, the measurements carried out on the samples for \(f = 1\) are consistent with the previously determined law \(L_c = 0.32 + 1.07f\) (9). Figure 6 summarizes the results. The adhesive strengths obtained for the SiCN coatings are larger than for SiC. The general trend is described by a linear law \(L_c = -1.7 + 2.3f\) (dotted line). In addition, obvious differences are encountered in function of \(f\), at constant film thickness. An increase of NH₃ in the gas phase tends to improve the critical load. The results do not yet allow to correlate precisely such an increase with a better adhesive strength. As a matter of fact, the deposit is modified through its nature, hardness, stress and perhaps interaction with the substrate as a consequence of differences in the phase diagrams Fe-Si-C, Fe-Si-N.
Figure 6: Critical loads in function of thickness for various f values; △ f = 0.05, ○ f = 0.5 ■ SiC deposits f = 1 □ other f values.

In both cases, at the deposition conditions, reaction will occur leading to solid solutions of Si in Fe but in the former one up to some 20 at% Si with free C, in the later one up to no more than 3% and reactions will depend on the nitrogen pressure.

Mechanical properties of the films were approached by indentation. The values presented in table 2 are generally an average over 7 measurements coming from distant places. When carried out with a too low load large errors arise, when reaching 1N cracks appear. In order to get a good comparative indicator, hardness at infinite load was calculated (Hv corrected). No clear variation appears but one notes that SiC coating (f = 1) is harder than SiN coating (f = 0.05). This result is qualitatively consistent with the properties of bulk CVD SiC (28-32 GPa) and Si3N4 (21GPa) obtained from the same gas phase. Apparent Young's modulus from unloading depth curves (20) needs the knowledge of the proportionality factor between the diagonal of the Vickers indentation (D) and the penetration depth (hR') measured from the non deformed surface, that is D/hR' which depends on the material tested.

Although no available value for the SiCN system, it is expected not far from 8, so two values (7 and 8) were considered on the basis of experimental data (20) (21). It comes out a fair variation in function of f: the end values are rather concordant with data for Si3N4 and SiC found in literature relative to CVD materials: respectively 300 GPa and 470 from Kamigaito (22).

Table 2: Indentation measurements of the coatings versus f

<table>
<thead>
<tr>
<th>GPa</th>
<th>f</th>
<th>0</th>
<th>0.05</th>
<th>1</th>
<th>0.3</th>
<th>0.5</th>
<th>0.75</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hv (0.5N)</td>
<td>36</td>
<td>47</td>
<td>39</td>
<td>55</td>
<td>43</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hv corrected</td>
<td>22.6</td>
<td>26.3</td>
<td>33</td>
<td>28</td>
<td>26.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E/(1-ν²)</td>
<td>-7</td>
<td>295</td>
<td>359</td>
<td>380</td>
<td>399</td>
<td>415</td>
<td>431</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-8</td>
<td>250</td>
<td>300</td>
<td>318</td>
<td>331</td>
<td>346</td>
<td>357</td>
<td></td>
</tr>
</tbody>
</table>

Concluding Remarks

The results of this study have demonstrated the possibility to obtain a continuous evolution of the composition of coatings in the system Si-C-N by properly managing the input gas phase: TMS-NH3-A. The gaseous C/N ratio governs the deposit composition. For these thick coatings, through different analysis, it has been seen that EPMA leads to an excess of nitrogen which is not confirmed by other methods. On an other hand XPS measurements are thought to give carbon contents by excess as we got some contamination (presence of oxygen). According to XPS the lines profiles show that the chemical environments of the three elements are more complicated than a mixture situation. A clear trend is observed indicating that various bonding states would be present. Considering the amorphous structure of the samples, this is not surprising. But, a further discussion to estimate in detail the bonding arrangements and uniformity in the films implies to carry out other studies. Variation in the composition of the thick films results in changing mechanical properties such as hardness, Young's modulus and also adhesion on the steel substrate.
In regards to our previously SiC based films, the incorporation of nitrogen lowers the hardness and the apparent Young's modulus with no fundamental change in adhesion. By that way, adherent coatings either Si3N4, SiCN or SiC rich in silicon can be obtained onto steel without the need of an intermediate layer. This system enables optimization studies in different fields: structure, adherence, and properties.

References