TiN-TixSiy Codeposits A.P.C.V.D. Produced Using the TiCl4-N2-SiH2Cl2-H2 System
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TiN-Ti<sub>x</sub>Si<sub>1-y</sub> Codeposits A.P.C.V.D. Produced Using the TiCl<sub>4</sub>-N<sub>2</sub>-SiH<sub>2</sub>Cl<sub>2</sub>-H<sub>2</sub> System

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Abstract. Mixtures of TiN<sub>x</sub>, TiS<sub>i</sub> and Ti<sub>5</sub>S<sub>i</sub>(N) were chemically vapour codeposited at atmospheric pressure using the TiCl<sub>4</sub> - N<sub>2</sub> - SiH<sub>2</sub>Cl<sub>2</sub> - H<sub>2</sub> system. Compact materials with very intimately dispersed phases and with controlled composition were obtained between 825 - 875°C and using flow rate ranges : 0.5 ≤ D<sub>N2</sub> ≤ 2.5, and 0.05 ≤ D<sub>SiH2Cl2</sub> ≤ 0.2 (in l/h). D<sub>TiCl4</sub> and D<sub>H2</sub> were kept constant at 0.183 and 30 (in l/h) respectively. According to the Ti-Si-N ternary phase diagram, TiNx with x = 0.95 ± 0.05, TiS<i</i> and Ti<sub>5</sub>S<i</i>(N), corresponding to some solubility of nitrogen into Ti<sub>5</sub>S<i</i>, were in thermodynamical equilibrium. At 850°C, D<sub>TiCl4</sub> = 0.183 and D<sub>H2</sub> = 30 (in l/h), the effect of N<sub>2</sub> and SiH<sub>2</sub>Cl<sub>2</sub> input concentrations were studied. At D<sub>SiH2Cl2</sub> = 0.1 l/h, the deposition rate was found to increase linearly with the square root of the N<sub>2</sub> molar fraction up to 5.10<sup>-2</sup>, then to decline at higher concentration. TiN<sub>x</sub> was 20 mol% at D<sub>N2</sub> = 0.5 l/h, reached about 40 mol% at 1 l/h and remained almost constant while D<sub>N2</sub> increased to 2 l/h. At D<sub>N2</sub> = 2 l/h, about 70 mol% in TiN<sub>x</sub> was obtained with D<sub>SiH2Cl2</sub> = 0.05 l/h. Then from D<sub>SiH2Cl2</sub> ranging from 0.1 to 0.2 l/h, TiN<sub>x</sub> concentration remains almost equal to 35 mol%. A linear dependence in the SiH<sub>2</sub>Cl<sub>2</sub> concentration was observed for the growth rate. The relationship between the logarithmic plot of the growth rate versus the reciprocal of codeposition temperature (in Kelvin) was linear and an apparent activation energy of 105 kJ/mol was calculated. The effect of temperature on the TiN<sub>x</sub> preferred orientations was also evidenced.

1. INTRODUCTION

The Ti-N-Si system is technologically interesting because of the properties of several of its compounds. TiN layers are particularly attractive because of their wear-resistance [1-2], erosion and abrasion-resistance [3-4], thermal stability, diffusion barrier applications [5-6], electroconductivity. But besides these positive properties, TiN coatings suffer from brittleness, as well as the other ceramics, and all the more, from limited oxidation resistance [7-11]. An improvement of these behaviours could be to incorporate titanium silicides in TiN by chemical vapour deposition. On one hand, the toughening effect of particule dispersion in a ceramic matrix is well established [12-14]. On the other hand, the oxidation resistance of titanium silicides is well known [15-16]. Two TiN-Ti<sub>x</sub>Si<sub>y</sub> deposited materials were already described. A film for semiconductor manufacture produced by OMCVD at low pressure and temperature using Ti[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> and an organic silane source [17]. An hard and very thin coating prepared by reactive sputtering process from a Ti<sub>x</sub>S<sub>y</sub> target in a Ar-N<sub>2</sub> gas mixture[18]. More recently, an amorphous film corresponding to Si incorporation in TiN was chemical vapour deposited from tetraakis (diethylamino) Ti - NH<sub>3</sub>-SiH<sub>4</sub> mixture [19]. The objective of this present work was to prepare thick and compact TiN-Ti<sub>x</sub>Si<sub>y</sub> composites by chemical vapour deposition. The mixture was TiCl<sub>4</sub> - N<sub>2</sub> - SiH<sub>2</sub>Cl<sub>2</sub> - H<sub>2</sub> and has never been used for this type of codeposition. This paper reports on the effect of the experimental parameters on the growth rate and phase composition of the codeposits.

2. EXPERIMENTAL PROCEDURE

Deposits were prepared by conventional thermal CVD, under atmospheric pressure. The reactor chamber consisted of a vertical silica tube (ϕ= 6.2 cm, L = 20 cm). The codeposition was onto mechanically polished crystalline graphite substrate (Le Carbone-Lorraine 1116 T; thickness=1.2 mm; thermal expansion coefficient = 6.10<sup>-6</sup> °C<sup>-1</sup>) resistivily heated. The substrate shape was designed to obtain a uniformly heated.
zone of 25x5 mm² (fig. 1). The temperature was P.I.D regulated and measured with a thermocouple (TKI). Liquid TiCl₄, gaseous SiH₂Cl₂ and N₂ in hydrogen were used as reactant sources. The principle of the gas distribution system is given in figure 1.

The TiCl₄ flow rate was calculated from its partial pressure imposed by the regulated temperature of a column through which flowed the hydrogen stream saturated with TiCl₄ after to be bubbled through heated liquid TiCl₄. Samples of different compositions were prepared by varying both the deposition temperature and the flow rates of the input gas species (Dₙ₂, Dₘ₄H₂Cl₂, Dₙ₂Cl₄ and Dₜ₂). The process time was chosen of 1 or 2 hours in order to obtain a thickness deposit of at least 40 μm.

The surface morphology of the polished cross sections and surface deposits was observed using an optical microscope and a scanning electron microscope. After having verified that the growth rates were almost independent of time, deposition rate was expressed in thickness per hour. The elemental compositions were obtained from photoelectron spectroscopy measurements carried out using a Riber SIA-200 spectrometer equipped with a monochromatic Al Kα X-ray radiations source: 1486.6 eV. Calibration was based upon the Cl₃ photoelectron peak of adventitious carbon at 284.6 eV. The relative intensities of the Ti 2p, Si 2p and N 1s peaks were used for the quantitative evaluations. The nature of the crystalline phases was determined by X-ray diffraction (Philips PW 1710, Cu Kα: 1.5418 Å).

3. RESULTS AND DISCUSSION

3.1 Multiphased codeposits

Samples of different compositions were prepared by varying both the codeposition temperature and concentrations of the input gas species. Temperature was varied between 800 to 1000°C and the variation ranges of the different flow rates were: 0.5 ≤ Dₙ₂ ≤ 2.5, and 0.05 ≤ Dₘ₄H₂Cl₂ ≤ 0.2. Dₙ₂Cl₄ and Dₜ₂ were kept constant at 0.183 and 30 (in l/h) respectively. All deposits were crystalline and have a colour ranged from yellow gold to light grey. Whatever the experimental conditions at least two phases were identified from their X-ray diffraction lines: the non-stoichiometric compound Tiₙₓ and Ti₅Si₃(N) corresponding to some solubility of nitrogen into Ti₅Si₃ [20-22]. In addition, depending mainly on the temperature of codeposition, Ti₅Si₂ was detected in some samples. The X-ray diffraction lines corresponding to Ti₅: 111, 200, 220, 311, 222 and 420, were assigned by comparison with those listed in the JCPDS file no.6-0642 (cubic system - Fm3m). The X-ray reflections of Ti₅Si₂ (orthorhombic system - Fddd; JCPDS file no.35-785) were identified in the samples prepared above 850°C. Whatever the
codeposition temperature (825-950°C), the X-ray diffraction pattern of Ti₅Si₃(N), corrected using TiSi₂ as an internal reference, was unambiguously attributed by comparison with that of Ti₅Si₃ (hexagonal system - P6₃/mcm; JCPDS file no. 29-1362). Because of dissolution of some amount of nitrogen, there were slight shifts of the X-ray reflections and modifications of the intensity lines (table I). These modifications, however, could also arise from the presence of a preferred orientation of the crystals. As a matter of fact, the strongest diffraction line was (002) for codeposits obtained in the range 825-900°C (table I) instead of (012) above 900°C.

Table 1: X-ray diffraction lines of Ti₅Si₃(N) corresponding to a codeposit prepared at: 850°C, DN₂ = 1.5, DSiH₂Cl₂ = 0.1, DTiCl₄ = 0.183 and DH₂ = 30 (in l/h).

<table>
<thead>
<tr>
<th>d (A)</th>
<th>I/I₀</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.587</td>
<td>100</td>
<td>002</td>
</tr>
<tr>
<td>2.402</td>
<td>35</td>
<td>012</td>
</tr>
<tr>
<td>2.210</td>
<td>3</td>
<td>121</td>
</tr>
<tr>
<td>1.490</td>
<td>6</td>
<td>123</td>
</tr>
<tr>
<td>1.294</td>
<td>46</td>
<td>004</td>
</tr>
<tr>
<td>1.222</td>
<td>2</td>
<td>240</td>
</tr>
</tbody>
</table>

From several spectra, average lattice parameters values of an hexagonal cell were calculated: a = 0.7424 ± 0.0008 nm and c = 0.517 ± 0.004 nm. In the same way, an average value, a = 0.4238 ± 0.0003 nm of the lattice parameter of Ti₅Nx was evaluated. From the experimentally established relationships between the lattice parameter and the nitrogen-titanium ratio [23-24], x was found of about 0.95 ± 0.05.

These results are consistent with the fact that according to the Ti-Si-N ternary phase diagram, Ti₅Nx, TiSi₂ and Ti₅Si₃(N) are in equilibrium. In the isothermal section represented in figure 2, the compatibility relationships between TiN and Si, Si₃N₄ and TiSi₂ originally selected by Beyers et al. [25] were complicated by the inclusion of recent data experimental established [21-22]. The stoichiometric range of Ti₅Nx is 0.53 < x < 1.14, Ti₂N and four titanium silicides: Ti₃Si, Ti₅Si₃, Ti₅Si₄, TiSi and TiSi₂ were taken into account. A solid solution Ti₅Si₃ (N) was assumed to equilibrate with Ti₅Si₄, TiSi and TiSi₂. In the three-phase equilibrium among Ti₅Si₃ (N)-TiSi₂-Ti₅Nx, x is close to 1, in agreement with our results. The fact that the lattice parameters of Ti₅Si₃ (N) were slightly larger than those of Ti₅Si₃ coexisting with Ti₅Si₄ i.e. a = 0.7422 nm and c = 0.51293 nm [20] was consistent with the nitrogen solubility.

The phase compositions of codeposits prepared between 825-875°C were evaluated by plotting the elemental compositions determined by XPS in the isothermal section (figure 2). Taking into account that Ti₅Si₃ dissolves about 10 at.% at 1100°C, [22] we assumed a solubility of 5 at%.
3.2 Effect of the experimental factors:

Codeposits were prepared at atmospheric pressure and the influence of temperature and gas flow rates was studied in order to achieve dense materials with very intimately dispersed phases and of coarse with controlled composition.

From preliminary experiments performed at the initial conditions: $D_{N_2} = 2$, $D_{SiH_2Cl_2} = 0.1$, $D_{TiCl_4} = 0.183$ and $D_{H_2} = 30$ (in l/h), we concluded that this main objective could be reached if the temperature was lower than 875°C. Below 825°C, the substrate was still incompletely covered after one hour of codeposition. Hence, the temperature was varied between 825°C to 875°C. From additional experiments done at 850°C taking twice less or more as 0.183 l/h of $D_{TiCl_4}$, it appeared that the quality of the coatings was poor. Therefore, this initial $TiCl_4$ flow rate was chosen for all the experiments.

3.2.1 Effect of the $N_2$ input concentration

Keeping constant all the other initial factors, the effect of $D_{N_2}$ was studied at 850°C in the range 0.5 - 2 l/h. The deposition rate was found to increase linearly with the square root of the $N_2$ molar fraction up to $X_{N_2} = 5 \times 10^{-2}$, then to decline at higher concentration (figure 3). The same dependence was already observed in the case of the deposition of $TiN$ [26-28].

![Figure 3: Growth rate of codeposits as a function of the $N_2$ input concentration. ( $D_{SiH_2Cl_2}=0.1$, $D_{TiCl_4}=0.183$ and $D_{H_2}=30$ (in l/h), $t^\circ C=850^\circ C$ )](image)

The $TiN$ concentration in the codeposits was 20 mol% at 0.5 l/h, reached about 40 mol% at $D_{N_2} = 1$ l/h and remained almost constant while $D_{N_2}$ increased to 2 l/h.

3.2.2 Effect of the $SiH_2Cl_2$ input concentration

To prepare $TiN$-rich composite, it was necessary to decrease the initial concentration in $SiH_2Cl_2$. At 850°C and $D_{N_2} = 2$, $D_{H_2} = 30$ (l/h), a codeposit of about 70 mol% in $TiN$ was obtained with $D_{SiH_2Cl_2}=0.05$ l/h. Then from $D_{SiH_2Cl_2}$ ranging from 0.1 to 0.2 l/h the $TiN$ concentration remains almost equal to 35 mol% (figure 4).

![Figure 4: $TiN$ concentration of the codeposits as a function of the $SiH_2Cl_2$ input concentration. ( $D_{N_2} = 2$, $D_{TiCl_4} = 0.183$ and $D_{H_2} = 30$ (in l/h), 850°C )](image)
For the growth rate a linear dependence in the SiH$_2$Cl$_2$ concentration seems to be observed (figure 5) while the N$_2$ molar fraction remains almost equal to 6.10$^{-2}$. The increasing of the thickness per hour is flat up to 3.10$^{-3}$ then high over 4.10$^{-4}$. In the first range, the deposition seems to be controlled by the N$_2$ input concentration. The coating thickness remains constant at about 30-35 μm and also the TiN concentration at about 32-38 mol%. Whereas in the second range, the deposition seems to be controlled by the SiH$_2$Cl$_2$ input concentration. The thickness increases significantly and also the quantities of the codeposited titanium silicides.

Figure 5: Growth rate of the codeposits as a function of the SiH$_2$Cl$_2$ input concentration. ( D$_{N2} = 2$, D$_{TiCl4} = 0.183$ and D$_{H2} = 30$ (in l/h), 850°C )

3.2.3 Effect of the temperature of codeposition

The effect of the temperature in the range 825-950°C was studied at: D$_{N2} = 2$, D$_{SiH2Cl2} = 0.1$, D$_{TiCl4} = 0.183$ and D$_{H2} = 30$ (in l/h). Above 875°C the quality of the codeposits was very poor but it was possible to follow the evolution of the titanium silicides from X-ray analysis. The ratio of the intensities of the strongest lines (311) for TiSi$_2$ and (012) or (002) for Ti$_5$Si$_3$(N) was evaluated. Figure 6 shows that the quantity of TiSi$_2$ increases with temperature at the expense of Ti$_5$Si$_3$(N).

Figure 6: The ratio of the intensities of the strongest lines (311) for TiSi$_2$ and (012) or (002) for Ti$_5$Si$_3$(N) in function of the temperature of codeposition.

The relationship between the logarithmic plot of the growth rate versus the reciprocal of codeposition temperature (in Kelvin) was linear (figure 7). From the slope of the fitted least square line, an apparent activation energy of 105 kJ/mol was calculated which is high enough to suggest that the process is controlled by surface kinetics. This value is in the range 84-101 kJ/mol of the experimental apparent activation energies corresponding to the chemical vapour deposition of TiN from TiCl$_4$-N$_2$-H$_2$ [29-30].
Figure 7: Logarithmic plot of the growth rate versus the reciprocal of codeposition temperature (in Kelvin). \( D_{N_2} = 2 \), \( D_{SiH_2Cl_2} = 0.1 \), \( D_{TiCl_4} = 0.183 \) and \( D_{H_2} = 30 \) (in l/h); temperature in the range 825-950°C.

The crystallographic orientations determined by XRD showed that (111), (200), (220), (311) and (420) orientations of TiNx were predominantly encountered in all codeposits. Taking into account these five main reflections, texture coefficients, \( t_{(hkl)} \) were calculated following the method of Harris [31]:

\[
t_{(hkl)} = \frac{I_{exp(hkl)} / I_{f(hkl)}}{1/n \sum I_{exp(hkl)} / I_{f(hkl)}}
\]

with the number of reflections \( n = 5 \). \( I_{exp(hkl)} \) is the measured intensity of the reflection \( (hkl) \) and \( I_{f(hkl)} \) the intensity of the same reflection of the JCPDS powdered TiN (file no.6-0642) randomly deposited. A preferred orientation (311) was evidenced up to 900°C (figure 8). It decreased as the temperature of codeposition increased and at 950°C TiNx was almost randomly deposited.

CONCLUSION

Thick and compact coatings consisting in a dispersion of titanium silicides in TiN were prepared by CVD using the TiCl4 - N2 - H2 - SiH2Cl2 system at atmospheric pressure, between 825-875°C and with flow rates: \( 0.5 \leq D_{N_2} \leq 2.5 \), \( 0.05 \leq D_{SiH_2Cl_2} \leq 0.2 \), \( D_{H_2} = 30 \) and \( D_{TiCl_4} = 0.183 \) (in l/h). Despite some lacks concerning the dependence on the TiCl4 and H2 input concentrations of phase ratio and growth rate, codeposit composition was controlled by varying \( D_{N_2} \) and \( D_{SiH_2Cl_2} \). According to the Ti-Si-N ternary phase diagram, TiNx with \( x = 0.95 \pm 0.05 \), TiSi2 and Ti5Si3(N) were in thermodynamical equilibrium at the temperature of codeposition. The microstructures of these materials is examinating by TEM and HREM. The thermal stability of the codeposits at higher temperature will be studied and also the oxidation resistance. In addition, the effect of the Ti1xSi2y inclusion on the mechanical behaviour of TiNx will be examined.

References