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TiN-Ti_xSi_y Codeposits A.P.C.V.D. Produced Using the TiCl₄-N₂-SiH₂Cl₂-H₂ System

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Abstract. Mixtures of TiN_x, TiSi₂ and Ti₅Si₃(N) were chemically vapour codeposited at atmospheric pressure using the TiCl₄ - N₂ - SiH₂Cl₂ - H₂ system. Compact materials with very intimately dispersed phases and with controlled composition were obtained between 825 - 875°C and using flow rate ranges : $0.5 \leq D_{N_2} \leq 2.5$, and $0.05 \leq D_{SiH_2Cl_2} \leq 0.2$ (in l/h). D_{TiCl_4} and D_{H_2} were kept constant at 0.183 and 30 (in l/h) respectively. According to the Ti-Si-N ternary phase diagram, TiN_x with $x = 0.95 \pm 0.05$, TiSi₂ and Ti₅Si₃(N), corresponding to some solubility of nitrogen into Ti₅Si₃, were in thermodynamical equilibrium. At 850°C, $D_{TiCl_4} = 0.183$ and $D_{H_2} = 30$ (in l/h), the effect of N₂ and SiH₂Cl₂ input concentrations were studied. At $D_{SiH_2Cl_2} = 0.1$ l/h, the deposition rate was found to increase linearly with the square root of the N₂ molar fraction up to $5 \cdot 10^{-2}$, then to decline at higher concentration. TiN_x was 20 mol% at $D_{N_2} = 0.5$ l/h, reached about 40 mol% at 1 l/h and remained almost constant while D_{N_2} increased to 2 l/h. At $D_{N_2} = 2$ l/h, about 70 mol% in TiN_x 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, TiN_x concentration remains almost equal to 35 mol%. A linear dependence in the SiH₂Cl₂ 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_x 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 codeposition. 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_xSi_y deposited materials were already described. A film for semiconductor manufacture produced by OMCVD at low pressure and temperature using Ti[N(CH₃)₂]₄ and an organic silane source [17]. An hard and very thin coating prepared by reactive sputtering process from a Ti_xSi_y target in a Ar-N₂ gas mixture [18]. More recently, an amorphous film corresponding to Si incorporation in TiN was chemical vapour deposited from tetrakis (diethylamino) Ti - NH₃-SiH₄ mixture [19].

The objective of this present work was to prepare thick and compact TiN-Ti_xSi_y composites by chemical vapour deposition. The mixture was TiCl₄ - N₂ - SiH₂Cl₂ - H₂ 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 ($\phi = 6.2$ 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 = $6 \cdot 10^{-6}$ °C⁻¹) resistively heated. The substrate shape was designed to obtain a uniformly heated

zone of $25 \times 5 \text{ mm}^2$ (fig.1). The temperature was P.I.D regulated and measured with a thermocouple (TKI). Liquid TiCl_4 , gaseous SiH_2Cl_2 and N_2 in hydrogen were used as reactant sources. The principle of the gas distribution system is given in figure 1.

Figure 1: Experimental arrangement and shape of the graphite substrate (1: reactor, 2: Joule heating line, 3: thermocouple, 4: liquid nitrogen trap, 5: Pirani gauge, 6: pressure regulating valve, 7: vacuum pump, 8: dew - point column, 9-10-11: mass flow - meters).

The TiCl_4 flow rate was calculated from its partial pressure imposed by the regulated temperature of a column through which flowed the hydrogen stream saturated with TiCl_4 after to be bubbled through heated liquid TiCl_4 . Samples of different compositions were prepared by varying both the deposition temperature and the flow rates of the input gas species (DN_2 , DSiH_2Cl_2 , DTiCl_4 and DH_2). The process time was chosen of 1 or 2 hours in order to obtain a thickness deposit of at least $40 \mu\text{m}$.

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 $\text{Al K}\alpha$ X-ray radiations source: 1486.6 eV. Calibration was based upon the C1s photoelectron peak of adventitious carbon at 284.6 eV. The relative intensities of the Ti2p , Si2p and N1s peaks were used for the quantitative evaluations. The nature of the crystalline phases was determined by X-ray diffraction (Philips PW 1710, $\text{Cu K}\alpha$: $1.5418 \text{ \AA}$).

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: $0.5 \leq \text{DN}_2 \leq 2.5$, and $0.05 \leq \text{DSiH}_2\text{Cl}_2 \leq 0.2$. DTiCl_4 and DH_2 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 TiN_x and $\text{Ti}_5\text{Si}_3(\text{N})$ corresponding to some solubility of nitrogen into Ti_5Si_3 [20-22]. In addition, depending mainly on the temperature of codeposition, TiSi_2 was detected in some samples. The X-ray diffraction lines corresponding to TiN_x : 111, 200, 220, 311, 222 and 420, were assigned by comparison with those listed in the JCPDS file no.6-0642 (cubic system - $\text{Fm}\bar{3}\text{m}$). The X-ray reflections of TiSi_2 (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 $\text{Ti}_5\text{Si}_3(\text{N})$, corrected using TiSi_2 as an internal reference, was unambiguously attributed by comparison with that of Ti_5Si_3 (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 1). 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 1) instead of (012) above 900°C.

Table 1: X-ray diffraction lines of $\text{Ti}_5\text{Si}_3(\text{N})$ corresponding to a codeposit prepared at: 850°C, $D_{\text{N}_2} = 1.5$, $D_{\text{SiH}_2\text{Cl}_2} = 0.1$, $D_{\text{TiCl}_4} = 0.183$ and $D_{\text{H}_2} = 30$ (in l/h).

d (Å)	I/I ₀	hkl
2.587	100	002
2.402	35	012
2.210	3	121
1.409	6	123
1.294	46	004
1.222	2	240

From several spectra, average lattice parameters values of an hexagonal cell were calculated : $a = 0.7424 \pm 0.0008$ nm and $c = 0.517 \pm 0.004$ nm. In the same way, an average value, $a = 0.4238 \pm 0.0003$ nm of the lattice parameter of TiN_x 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 .

Figure 2: Ti-Si-N isothermal section and the plotted elemental compositions of codeposits prepared at atmospheric pressure, temperature range: 825 - 875°C; $0.5 \leq D_{\text{N}_2} \leq 2.5$, $0.05 \leq D_{\text{SiH}_2\text{Cl}_2} \leq 0.2$, $D_{\text{H}_2} = 30$, $D_{\text{TiCl}_4} = 0.183$ (in l/h).

These results are consistent with the fact that according to the Ti-Si-N ternary phase diagram, TiN_x , TiSi_2 and $\text{Ti}_5\text{Si}_3(\text{N})$ are in equilibrium. In the isothermal section represented in figure 2, the compatibility relationships between TiN and Si , Si_3N_4 and TiSi_2 originally selected by Beyers et al. [25] were complicated by the inclusion of recent data experimentally established [21-22]. The stoichiometric range of TiN_x is $0.53 < x < 1.14$, Ti_2N and four titanium silicides: Ti_3Si , Ti_5Si_3 , Ti_5Si_4 , TiSi and TiSi_2 were taken into account. A solid solution $\text{Ti}_5\text{Si}_3(\text{N})$ was assumed to equilibrate with Ti_5Si_4 , TiSi and TiSi_2 . In the three-phase equilibrium among $\text{Ti}_5\text{Si}_3(\text{N})$ - TiSi_2 - TiN_x , x is close to 1, in agreement with our results. The fact that the lattice parameters of $\text{Ti}_5\text{Si}_3(\text{N})$ were slightly larger than those of Ti_5Si_3 coexisting with Ti_5Si_4 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 Ti_5Si_3 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 $X_{N_2} = 5 \cdot 10^{-2}$, 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), $t^\circ\text{C}=850^\circ\text{C}$)

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)

For the growth rate a linear dependence in the SiH_2Cl_2 concentration seems to be observed (figure 5) while the N_2 molar fraction remains almost equal to $6 \cdot 10^{-2}$. The increasing of the thickness per hour is flat up to $3 \cdot 10^{-3}$ then high over $4 \cdot 10^{-4}$. 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_2Cl_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_2Cl_2 input concentration. ($D_{\text{N}_2} = 2$, $D_{\text{TiCl}_4} = 0.183$ and $D_{\text{H}_2} = 30$ (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: $D_{\text{N}_2} = 2$, $D_{\text{SiH}_2\text{Cl}_2} = 0.1$, $D_{\text{TiCl}_4} = 0.183$ and $D_{\text{H}_2} = 30$ (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 $\text{Ti}_5\text{Si}_3(\text{N})$ was evaluated. Figure 6 shows that the quantity of TiSi_2 increases with temperature at the expense of $\text{Ti}_5\text{Si}_3(\text{N})$.

Figure 6: The ratio of the intensities of the strongest lines (311) for TiSi_2 and (012) or (002) for $\text{Ti}_5\text{Si}_3(\text{N})$ 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). ($DN_2 = 2$, $DSiH_2Cl_2 = 0.1$, $DTiCl_4 = 0.183$ and $DH_2 = 30$ (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 TiN_x were predominantly encountered in all codeposits. Taking into account these five main reflections, texture coefficients, $t_c(hkl)$ were calculated following the method of Harris [31]: $t_c(hkl) = [I_{exp}(hkl)/I_r(hkl)] / 1/n \sum [I_{exp}(hkl)/I_r(hkl)]$ with the number of reflections $n = 5$. $I_{exp}(hkl)$ is the measured intensity of the reflection (hkl) and $I_r(hkl)$ 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 TiN_x was almost randomly deposited.

Figure 8: Texture coefficients of TiN_x in function of the codeposition temperature.

CONCLUSION

Thick and compact coatings consisting in a dispersion of titanium silicides in TiN were prepared by CVD using the $TiCl_4 - N_2 - H_2 - SiH_2Cl_2$ system at atmospheric pressure, between 825-875°C and with flow rates: $0.5 \leq DN_2 \leq 2.5$, $0.05 \leq DSiH_2Cl_2 \leq 0.2$, $DH_2 = 30$ and $DTiCl_4 = 0.183$ (in l/h). Despite some lacks concerning the dependence on the $TiCl_4$ and H_2 input concentrations of phase ratio and growth rate, codeposit composition was controlled by varying DN_2 and $DSiH_2Cl_2$. According to the Ti-Si-N ternary phase diagram, TiN_x with $x = 0.95 \pm 0.05$, $TiSi_2$ and $Ti_5Si_3(N)$ were in thermodynamical equilibrium at the temperature of codeposition. The microstructures of these materials is examining 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 Ti_xSi_y inclusion on the mechanical behaviour of TiN_x will be examined.

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