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Plasma-enhanced chemical vapour deposition of silicon nitride from $SiCl_4$, nitrogen and hydrogen on hard metals

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Silicon nitride coatings were deposited on hard metals at a reaction temperature between 873 and 1173 K by a plasma-enhanced chemical vapour deposition process operating with an r.f. discharge. The dependence of the coatings on the process parameters (deposition temperature and r.f. power) was investigated, in respect of phase composition, impurities in the coatings, metallographic appearance, microhardness, adhesion and layer-substrate interaction. It was found that upto a deposition temperature of 1023 K the coatings were amorphous. Above 1023 K the coatings increasingly contained crystalline regions. At 1173 K and an r.f. power above 200 W, the coatings were nearly completely crystalline.

1. Introduction

Silicon nitride is a material with a great variety of applications. As laminated material it is used to a high degree in microelectronics [1]. Because of its relatively great hardness and its chemical and oxidation resistance, however, its use as a wear-resistant coating [2] and as anti-corrosive or thermostable layer [3] is also possible.

In order to investigate the wear resistance of silicon nitride layers, the dependence of structure and some other properties on the conditions of the chemical vapour deposition (CVD) processes, especially on temperature, were explored. Because of the restrictions of the relatively high deposition temperature required [4], it is not possible in the conventional CVD process to succeed in avoiding interactions of the components of the hard metal, especially of the binder phase forming silicide [5, 6]. Therefore, a plasma-enhanced CVD process was employed enabling coating temperatures below 1200 K to be used.

2. Experimental procedure

2.1. Plasma-enhanced CVD process

The stainless steel coaxial reactor used, with capacitive feeding of the r.f. power, is shown schematically in Fig. 1. The reaction chamber (i.d. 50 mm) can be heated by an outer resistance furnace to, at most, 1223 K. The capacitive feeding of the r.f. power was realized by an 1 KW generator with a frequency of 4.05 MHz. Because of the significantly smaller area of the inner rod-shaped r.f. electrode in comparison to the earthed reactor wall acting as counter electrode, a negative bias voltage is applied to the inner electrode [7]. For this reason, a more powerful ion bombardment takes place.

$SiCl_4$, nitrogen and hydrogen were used as reactants. Argon could also be added to the gas mixture. All gases were purified by contact columns (palladium or nickel catalyst), molecular sieve columns and an aerosol filter. $SiCl_4$ was repeatedly distilled and fed directly into the reaction chamber by a liquid evaporator using hydrogen as carrier gas. Compared to ammonia, which is most frequently used, the use of nitrogen has the advantage of avoiding the formation of solid addition compounds between $SiCl_4$ and NH_3 in the reaction gas, and therefore of simplifying the reaction process. In this case, however, an additional activation of the less active nitrogen (high dissociation energy) by glow discharge is required to reach reaction temperatures below 1273 K.

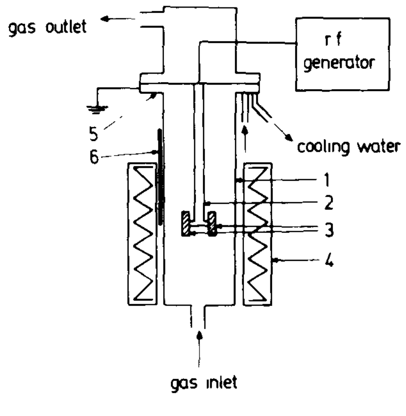

Figure 1 Plasma-enhanced CVD coaxial reactor with capacitive feeding of the r.f. power. 1, ground steel tube, 2, r.f. rod electrode with substrate holder; 3, substrates, 4, furnace; 5, water-cooled flange; 6, thermocouple.

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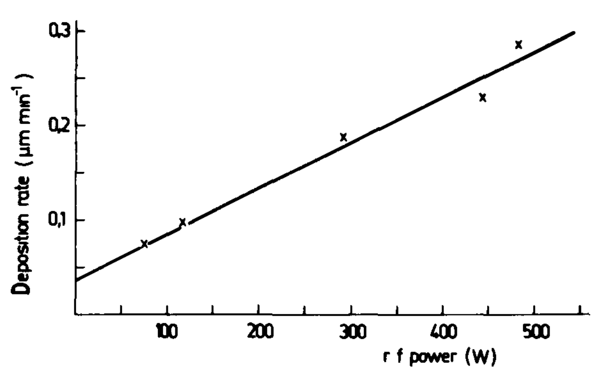

Figure 2 Dependence of the deposition rate of silicon nitride on the r.f. power (substrate temperature 1123 K, WC/Co substrate).

2.2. Deposition conditions

Experiments were carried out in the temperature range 873 to 1173 K, at a pressure of 530 Pa and an r.f. power between 50 and 400 W. The $SiCl_4$ flow rate through the reactor amounted to 1.6×10^{-2} mol h^{-1} at 530 Pa. The molar ratios, n_H/n_{Si} and n_N/n_{Si}, were 6 and about 200, respectively.

As demonstrated in Fig. 2, in the range considered an approximately linear correlation exists between the deposition rate and the r.f. power.

3. Results and discussion

3.1. Characterization of the coatings

3.1.1. Metallographic investigations and density of the coatings

Monophase, grey transparent coatings were obtained. Fig. 3 shows a micrograph of such a silicon nitride coating. The coatings adhere to hard metal substrates until at most a 7 µm layer thickness is reached, then delamination occurs, especially at the edges. The deposited layers could not be etched (liquid chemically) with fluoric acid and were insoluble in a solution of caustic soda. This indicates, in particular, the absence of free silicon.

For the determination of density, the coatings were deposited on an inert substrate (aluminium oxide

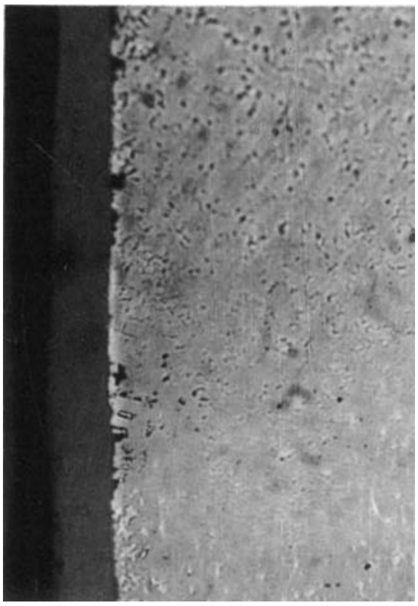

Figure 3 Homogeneous, monophase silicon nitride coating on WC/Co substrate (metallographic grinding).

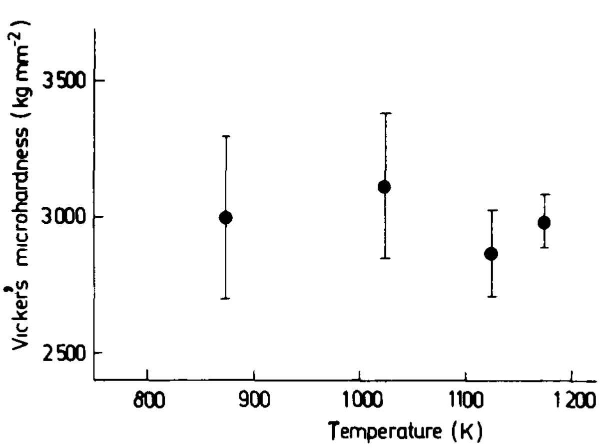

Figure 4 Dependence of the microhardness of the silicon nitride coatings on the deposition temperature.

plates). The densities obtained were 2.38 g cm^{-3} at a substrate temperature of 873 K and 3.06 g cm^{-3} at 1173 K. Chu *et al.* [8] reported a similar density trend, i.e. increasing density with rising substrate temperature and a theoretical density of α-Si_3N_4 of 3.18 g cm^{-3}.

3.1.2. Microhardness of the coatings

The microhardness of the coatings deposited was about 3000 Vickers units (29.4 GPa), independent of the deposition temperature which varied between 873 and 1273 K (see Fig. 4). Very different values of microhardness are given in the literature: between 2950 [9] and 4600 to 5000 Vickers units for fine-grained α-Si_3N_4 [10]. The microhardness of the coatings obtained in the present work using plasma-enhanced CVD coincide with the former value or are a little higher.

3.1.3. Phase analysis

From radiographic phase analysis it resulted that above 1023 K, α-Si_3N_4 and above 1073 K to a lesser degree also β-Si_3N_4 occur. Fig. 5 shows graphically the dependence of the limits for the deposition of the different phases on WC/Co hard metal substrates on deposition temperature and r.f. power. In all, three phase regions can be discerned in the parameter range

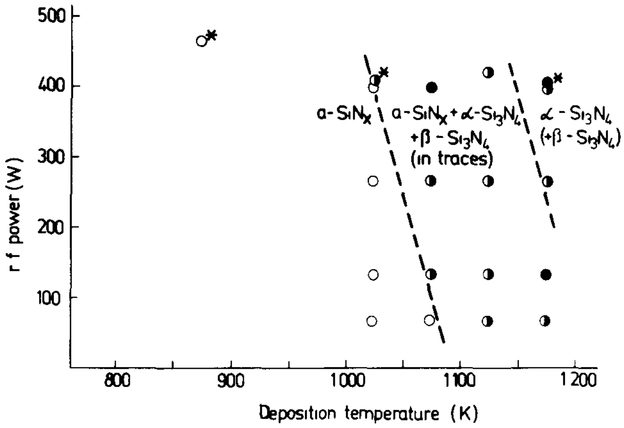

Figure 5 Dependence of the phase composition of the silicon nitride coatings on the deposition temperature and fed r.f. power. (○) Amorphous silicon nitride (a-SiN_x), (◑) layer containing α-Si_3N_4, (●) layer containing α-Si_3N_4 and traces of β-Si_3N_4, (*) WC/Co substrates precoated with TiN or Ti(C, N).

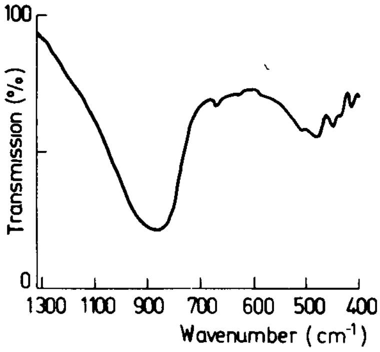

Figure 6 Infrared absorption spectrum of a silicon nitride layer deposited at 1023 K.

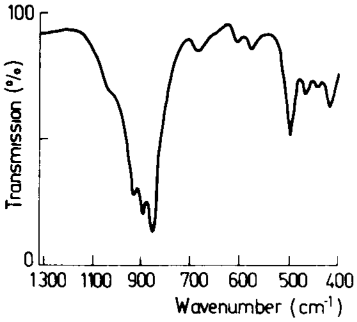

Figure 8 Infrared absorption spectrum of a silicon nitride layer deposited at 1173 K.

investigated: region 1 amorphous silicon nitride a-SiN_x, region 2 a-SiN_x/α-Si_3N_4/β-Si_3N_4 (in traces), region 3 α-Si_3N_4 or α-Si_3N_4/β-Si_3N_4. Apparently the deposition region of pure β-Si_3N_4 is located at a higher temperature, because in the temperature range investigated it has only been found to a low degree. However, the substrate also has an effect on the phase composition. Thus on a pure WC/Co hard metal, α-Si_3N_4 is deposited preferentially. Supplementary experiments at 1173 K and 400 W confirm that on hard metals precoated with a titanium nitride or titanium carbonitride layer, a mixture of α-Si_3N_4 and β-Si_3N_4 was deposited, with α-Si_3N_4 prevailing, in region 3 (nearly completely crystalline coatings), as is obvious from the infrared spectrum at 1173 K given below in Fig. 8, and from the electronmicroscopic image of the Si_3N_4-coating surface (see Fig. 10). The formation of cobalt silicide was not found in any sample.

3.1.4. *Infrared spectroscopic investigations*

In parallel with the phase analysis investigations, infrared transmission spectra of silicon nitride coatings were measured. For this purpose silicon nitride was deposited with a coating thickness of about 1 µm on silicon substrates at three different substrate temperatures and an r.f. generator power of 400 W. These infrared spectra are shown in Figs 6 to 8.

Fig. 6 shows a spectrum, which is nearly equivalent to published spectra of amorphous hydrogen-free silicon nitride [8, 11–13]. The Si–N band at 870 cm^{-1} is not split, but splitting is seen in the wide band at 500 cm^{-1}. The peak at 470 cm^{-1} is asymmetric, indicating an overlap with an as yet unresolved absorption at the shortwave edge of the band at 470 cm^{-1}.

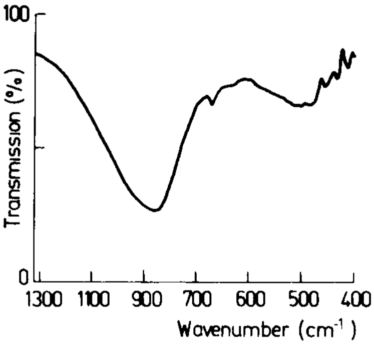

Figure 7 Infrared absorption spectrum of a silicon nitride layer deposited at 1123 K.

As shown in Fig. 7, a new band occurs at 500 cm^{-1}, and at 870 cm^{-1} a sharper peak appears in outline, thus the whole band becomes asymmetric, but it is not yet split into single peaks.

All absorption maxima occurring for the layer deposited at 1173 K (Fig. 8) are present in the spectrum of α-Si_3N_4 given by Wada *et al.* [13], reported with the following wavenumbers: 412, 440, 463, 499, 580, 600, 688, 874, 909 and 935 cm^{-1}.

In sputtered *a*-SiO_xN_y films an absorption at 1050 cm^{-1} is found, which is related to the Si–O valence vibration [11]. Therefore, this absorption, in contrast to Wada *et al.*'s observations [13] is related to the Si–O bond. In our spectra this absorption appeared only as a shoulder with significantly lower intensity. Si–H and N–H bands were not detectable, i.e. hydrogen is of no importance as a coating component. The spectra corroborate the results of the phase analysis and show that beginning at a deposition temperature of 1023 K, increasingly crystalline regions of α-Si_3N_4 exist in an amorphous matrix. At 1173 K, a nearly completely crystalline layer is deposited, consisting of α-Si_3N_4.

3.1.5. *Mass-spectrometric investigation*

Another potential impurity in addition to oxygen, is chlorine. Fig. 9 shows the dependence of the mass-spectroscopically determined chlorine content on the

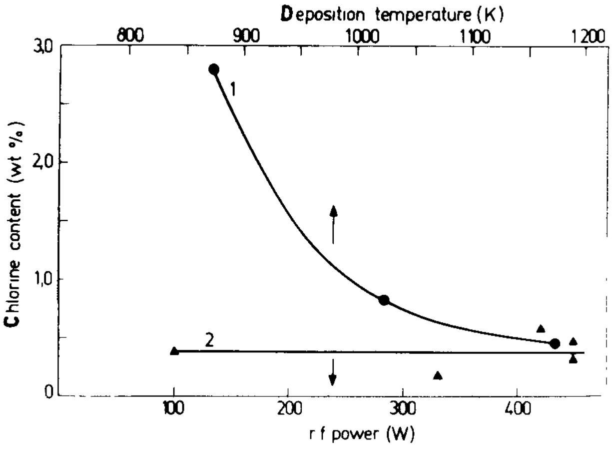

Figure 9 Dependence of the chlorine content of the silicon nitride coatings on the deposition temperature and r f. power.

deposition temperature and r.f. power. The silicon nitride coatings obtained at a constant r.f. power of 400 W show an evident dependence of the chlorine content on the substrate temperature (curve 1). The r.f. power, however, has no significant influence at constant substrate temperature ($T_s = 1173$ K). The results indicate that at low deposition temperatures, considerable amounts of chlorine still exist in the coatings. Only above 1023 K does the chlorine content diminish to less than 1 wt %.

In some samples the oxygen content was also determined mass-spectroscopically, which already had appeared in outline in the infrared spectra as an impurity. Values between 0.05 and 0.2 wt % were determined.

3.1.6. Adhesion of the coatings

The adhesion of the coatings was assessed by a scratch test. For this purpose silicon nitride coatings deposited at a deposition temperature of 1173 K on WC/Co substrates with a 10 μm thick titanium carbonitride layer were investigated. No large-area delamination caused by micro-spallings appeared. The critical load was 20 N. Fig. 10 illustrates such a scratch trace. The results demonstrate that these silicon nitride coatings have a good adhesion to the substrate, but they are hard and brittle, and obviously they are under a strong internal stress.

3.2. Layer-substrate transition

In the case of direct deposition on hard metals, no formation of cobalt silicide upto 1173 K was observed. This is ascertained both metallographically and by phase analysis. Additional tests in a quartz reactor at deposition temperatures higher than 1173 K have demonstrated that above 1273 K a cobalt silicide intermediate layer can be detected, which intensifies on further increasing the deposition temperature.

If the hard metals are precoated with a 10 μm thick titanium carbonitride layer, above 1373 K an interaction between the binder metal of the hard metal substrate and Si_3N_4 or silicon species of the gas phase, respectively, can be found. In this case the cobalt silicide layer is situated between the titanium carbonitride and the silicon nitride, i.e. cobalt diffuses through the intermediate layer and reacts at the beginning of the deposition of silicon nitride with the silicious gas phase species and the silicon nitride itself.

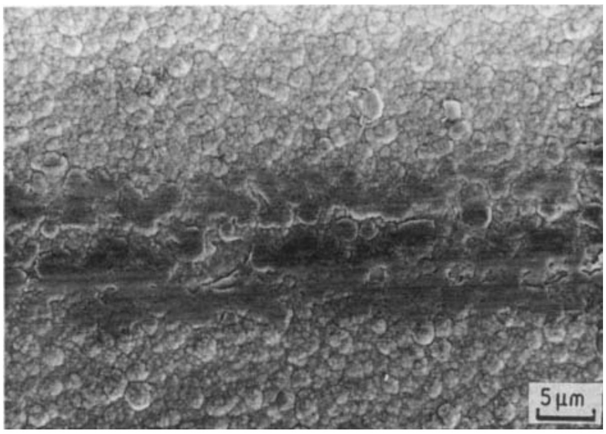

Figure 10 SEM image of the silicon nitride coating surface with a scratch trace.

From these results it follows that the substrate temperature of uncoated WC/Co substrate should not exceed 1173 K, and for substrates coated with titanium carbonitride it should be below 1373 K. Similar results concerning the hard metal coating with SiC have been obtained by Schintlmeister *et al.* [5].

4. Conclusion

For the Si–N–H–Cl system, silicon nitride coatings were deposited from the reactants $SiCl_4$, nitrogen and hydrogen at a reaction temperature between 873 and 1173 K, using a plasma-enhanced CVD process operating with an r.f. discharge. The characterization of the coatings was carried out by phase analysis, infrared spectroscopy and mass spectroscopy as well as by metallography. The following results were obtained.

1. Grey, homogeneous and transparent coatings were formed, adhering to WC/Co hard metal substrates up to a thickness of about 7 μm.
2. Up to a deposition temperature of 1023 K the coatings were amorphous. Above 1023 K the coatings increasingly contained crystalline regions of α-Si_3N_4 and to a lesser degree also β-Si_3N_4. At 1173 K and an r.f. generator power above 200 W, the coatings were nearly completely crystalline.
3. The microhardness of the silicon nitride coatings had a value of about 3000 Vickers units (29.4 GPa), independent of the deposition temperature which varied between 873 and 1173 K.
4. A direct coating of the WC/Co hard metals without the formation of silicide of the hard metal components was possible up to 1173 K. Precoating the hard metal with a 10 μm thick titanium carbonitride intermediate layer enabled coating to be achieved up to 1373 K.
5. The scratch test demonstrated that the silicon nitride layers failed by the formation of microdelaminations. This is probably caused by the brittleness of the coatings and by the existence of internal stress.

Acknowledgements

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