SOME NEW HARD COATINGS PREPARED BY PLASMA ENHANCED CVD USING ORGANOMETALLICS

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ABSTRACT

In a program to substitute $TiCl_4$, the commonly used precursor for hard coatings, by halogen free materials several organometallic compounds have been tested. Films of ZrN have been prepared from $Zr(N(C_2H_5)_2)_4$. For ZrB_2 films $Zr(BH_4)_4$, for VC films $V(C_5H_5)_2$, for SiC films $Si(Si(CH_3)_3)_4$, and for Al_2O_3 films $Al(OC_3H_7)_3$ and $Al(acac)_3$ served as precursors.

INTRODUCTION

Thin films of hard coatings are becoming increasingly important for high performance cutting and pressing tools. By far the most widely used hard coating material is TiN. The limitation to only a few materials is a consequence of the coating technique. Hard coatings are normally prepared by thermal or plasma CVD, both of which need volatile precursors. Since $TiCl_4$ is commercially available and has a high vapour pressure it has become the most important precursor for the thermal CVD and PECVD of hard coatings. $TiCl_4$ is, however, a highly corrosive material and the deposites prepared from this precursor might contain residual halogen which causes corrosion at the interphase to the substrate. Because of these disadvantages a program has been started to develop alternative CVD methods for hard coatings.

The prerequisite for all CVD processes (thermal, plasma or laser) is the availability of volatile precursors. Of the elements interesting for hard coatings only few form volatile compounds. For this reason research has concentrated on finding, developing and testing new volatile organometallics suitable as precursors for hard coatings. Recently some organometallic titanium compounds /1/ have been tested as possible substitutes for $TiCl_4$. But since there is a great variety of equally hard or even harder materials, the study has not been restricted to titanium compounds. We here report the deposition of ZrN, ZrB_2, VC, SiC and Al_2O_3.

EXPERIMENTAL

For all depositions parallel plate reactors were used with electrodes of 16 cm diameter and a spacing of 3 cm. The lower electrode which was bearing the substrates could be heated up to 673 K. The carrier gases after passing through the evaporation vessel entered the reactor through the upper electrode. In most experiments the lower electrode was at ground potential while the upper electrode was attached via a matching network to an rf - generator (13.56 MHz). For studies of the influence of bias the polarity was reversed. The films were analyzed by weight, talysurf, REM, IR, Auger spectroscopy, XPS, hardness measurements, dc four point probe measurements of the electrical resistivity. The metal content was determined by AAS or photometry /2/, the carbon content by a LECO CS 244 analyzer and the nitrogen content by photometry /3/.

RESULTS AND DISCUSSION

The hardness of titanium nitride as bulk material is 2100 Vickers. A comparison of hardness values showes that a number of materials have a similar or better Vickers hardness: (HV) ZrN 1600, HfN 1700, TiC 3000, VC 2900, SiC ≈3000, TiB_2 3400 $ZrB_2$2250, HfB_2 2900, Al_2O_3 ≈2600 HV /4,5/.

In a recent test of various titanium organic compounds $Ti(N(C_2H_5)_2)_4$ seemed especially promising /1/. But there are certain disadvantages with this precursor. Though the metal is surrounded by four nitrogen atoms, its decomposition leads to carbides and carbonitrides rather than to nitrides. Furthermore, the deposits always contain considerable amounts of oxygen. The impurities are caused by the oxygen sensitivity of the precursor and the growing film.

The difficulties encountered with the oxygen affinity of the titanium compound are not observed with $Zr(N(C_2H_5)_2)_4$. The compound has been used in CVD /6/ but never in PECVD. It is easy to handle, has a good stability, and can be vapourized at 383-393 K. With hydrogen as carrier gas, power, bias, and substrate temperature have been varied. As seen in Tab. 1 the results are fairly independent of the experimental conditions. Almost all films show Zr-contents > 80% and thus are coming close to the composition of ZrN (86.7% Zr). The nitrogen contents also approaches the value for ZrN. All films contain a few percent of carbon. The color of the deposits is brown - metallic, while bulk ZrN has a golden color. The difference is probably due to the few percent of carbon in the films.

Only at the lowest setting of power and bias the conversion of the precursor seems to be incomplete. All other parameter combinations lead to a composition $\approx ZrN_{0.9}C_{0.6}$. According to elemental analyses the deposits contain no oxygen. Auger spectra show a highly oxidized surface but very little oxygen in the film, XPS spectra show nitrogen in the range typical for nitrides. With increasing bias the electrical conductivity and the hardness of the deposits increased. The best values obtained without special optimisation are $1x10^3$ μΩcm for the resistivity and 1600 for the Knoop hardness which is somewhat lower than the reported value for the bulk material (2000 HV) /7/. The lowest substrate temperature at which hard and adherent ZrN-films could be deposited was 573 K, while in CVD-experiments /6/ 773 K was necessary.

substrate [°C]	power [W/cm2]	Bias [V]	Zr wt%	N wt%	C wt%
400	0.25	0	74.8	19.4	11.2
400	0.25	-220	81.2	10.8	7.5
400	0.5	-290	81.2	10.0	7.5
400	1	0	83.1	12.2	8.1
200	0.75	-380	82.6	9.5	5.3
300	1.25	0	82.0	11.4	4.4
300	0.75	-380	n.d.	10.8	6.9
400	1.25	0	80.7	14.5	4.8

Tab. 1 Deposition of ZrN_xC_y using $Zr(N(C_2H_5)_2)_4$ as precursor (ZrN 86.7% Zr)

The use of borides as hard coatings has been proposed in several recent reviews. TiB_2 films have been prepared from $TiCl_4$ + BCl_3 + H_2 by thermal CVD (at ≈133 K) and by PECVD at ≥750 K /8/. As alternative precursors Girolami has used the well known borohydride complexes /9/ and he was able to prepare films of TiB_2, ZrB_2, and HfB_2 by thermal CVD. The borohydrides have also been used in PECVD where the deposition rates were 1-2 orders of magnitude higher. The borohydrides are quite sensitive to moisture and oxygen and require special precautions in handling. Their high vapour pressure and the absence of carbon, however, makes them ideal precursors for the deposition of pure boride films.

In the PECVD experiments the influence of power, temperature of substrate and vapouriser have been studied. In the range of 263 - 313 K $Zr(BH_4)_4$ has sufficient high vapour pressure for CVD experiments. The deposition rate strongly increases with the vapour pressure of the precursor (Fig. 1). Only at the lowest rates the films were brown, transparent, and had no measurable electrical conductivity. At higher rates silvery metallic films resulted with metal contents of 70-75% Zr (ZrB_2 80.9% Zr) and resistivities of 400-500 µΩcm (ZrB_2 9 µΩcm). Spectroscopic data indicate a highly oxidized surface but no oxygen in the film. Similar results have been obtained with $Hf(BH_4)_4$ which yielded films of HfB_2.

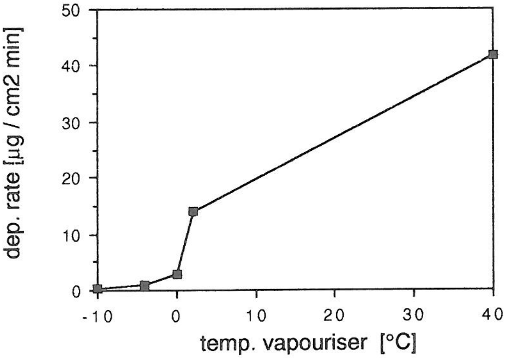

Figure 1 Deposition rate of ZrB_2 - films from $Zr(BH_4)_4$ as function of the temperature of the vapouriser.

Several carbides are interesting materials for hard coatings. Carbide films have been prepared by CVD using metal halides as precursors. Recently some organometallic compounds have been studied as possible alternatives. The thermal deposition of TiC - films using neopentyl-titanium has been reported /10/ but this compound suffers from a low shelf live. Some π-complexes also make interesting precursors. Using bis-η^5-cyclopenta-dienyl-vanadium (VCp_2, vanadocene) vanadium carbide could be deposited. VC - coatings have been grown by CVD on steel using VCl_2 /11/.

VCp_2 was chosen as alternative precursor, because it is thermally stable and sublimes over a wide temperature range (> 323 K, 20 Pa). It is, however, quite sensitive towards oxygen and thus requires special handling. In the PECVD experiments the precursor was vapourized at 333 K. With pure hydrogen at low flow rates the films contain only ≈ 40% V, 40%C and ≈20% O. With increasing hydrogen flow the composition of the film approaches the values of VC (Fig. 2). At the same time the conductivity increases to values of 5-6 x 10^3 µΩcm (VC 1.5×10^2 µΩcm). XPS spectra show only the $V2p_{2/3}$ and C1s signals of the carbide.

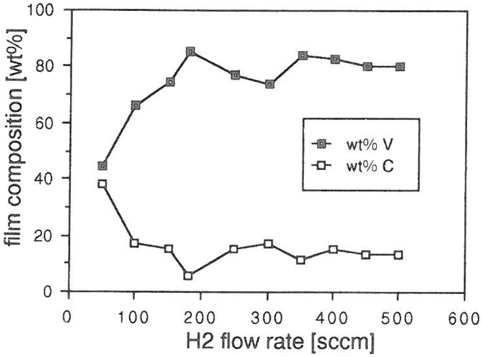

Figure 2 film composition as function of hydrogen flow (VC: 81.0% V)

Another interesting material is silicon carbide which combines hardness (Mohs 9.6) with chemical inertness. The formation of silicon carbide has been studied using $Si(Si(CH_3)_3)_4$ as precursor. This compound is especially easy to handle. It is stable against air and moisture and has already at 350 K a vapour pressure sufficient for CVD experiments. In almost all experiments colorless to yellow films were deposited with 30±3 % carbon (SiC 29.9 wt% C). There is an almost linear increase of the deposition rate with power. An increase in substrate temperature caused a decrease of deposition rate but led to films with a much better Knoop hardness (Figure 3). The best hardness values were 2200 (SiC 2480 H-Knoop).

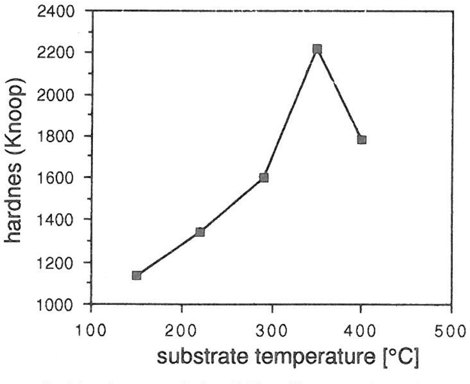

Figure 3 Hardness of the SiC - films as function of substrate temperature

Since most organometallic compounds react easily with oxygen, these compounds can also be used as precursors for the deposition of oxide films. However, if the oxygen affinity of the precursor is too great the oxidation might already occur in the gas phase. As hard coatings Al_2O_3 and ZrO_2 are of special interest because of their hardness being 9.5 and 7-9 Mohs respectively. The deposition of cubic ZrO_2 will be discussed in a separate paper /12/.

The alkyl derivatives of aluminium are very volatile but extremely sensitive to air and moisture. Other aluminum compounds are better to control. $Al(acac)_3$ and $Al(O\text{-}C_3H_7^i)_3$ can be vapourized at 440 K and yield amorphous, carbon free films of Al_2O_3 at substrate temperatures of 673 K. Details are being discussed in a seperate paper /12/.

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