Amorphous titanium carbide films were produced by low-temperature (<300°C) and low-pressure (<10^-3 Pa) metalorganic chemical vapor deposition from tetraneopentyl-titanium. X-ray and electron diffraction studies showed that the deposits were amorphous. The coatings were analyzed by Auger electron spectroscopy, electron energy loss spectroscopy, and electron spectroscopy for chemical analysis. The results of these studies suggest a deposition mechanism and lead to an understanding of the film morphology and microchemistry and the exceptional stability of the amorphous phase. It is believed that organic clusters and hydrogen, resulting from the decomposition of the Ti(tetrapeptide) molecule, are present in the TiC films, and that they probably play a major role in stabilizing the amorphous phase to higher temperatures (>1000°C) than typical glassy metals, in agreement with other studies of similar systems.

One of the advanced ceramic materials being considered for use as a protective coating under extreme chemical, thermal, and mechanical conditions is the refractory compound titanium carbide, TiC. In Japan and the U.S., TiC has been identified as a material of interest for the “first wall” coating for the fusion reactor. It is also being studied as a low-friction thermal barrier coating for cylinder walls in the adiabatic diesel engine.

In its crystalline form, which is NaCl structure, TiC is a hard, marmetallurgical high melting, chemically inert, low-friction material. These properties are currently exploited in CVD coatings for bearings and cutting tools. On the expectation that these properties might be further enhanced by TiC in an amorphous rather than crystalline form, we initiated a study of the preparation and characteristics of thin films of amorphous TiC. Following the procedure of Moranco et al., who employed Ti(bipy)_2, we formed amorphous films of TiC by metalorganic chemical vapor deposition (MOCVD) from selected organometallic compounds that carry Ti. The reason for choosing this approach is that molecules of such compounds dissociate at relatively low temperatures — 200°C to 400°C — compared with 1100°C to 1350°C for conventional CVD preparation of TiC from TiCl_4 and hydrocarbon. At lower substrate temperatures, thermal energy for the diffusional steps required in crystallization is not available (e.g. Ref. 8). In addition, the large molecular fragments remaining after the dissociation of the Ti-bearing molecule may become trapped in the TiC film and may interfere with crystallization. However, unlike Moranco et al., who prepared amorphous Ti-rich films which were not single-phase TiC, and unlike other workers, who produced amorphous TiC films incidentally to other goals, our purpose is to produce and study amorphous TiC films.

The present paper is one in a series of reports on the successful preparation of amorphous TiC films by low-temperature MOCVD. Results are presented for the organometallic compounds “tetraneopentyl-titanium,” which is different from the molecule “titanium bipyridine” used by Moranco et al. and by the present authors in initial studies. In particular, we show that crystallization of the amorphous TiC film produced does not occur until the temperature is raised above 1000°C — a result to be contrasted with the usual 300°C crystallization temperatures for glassy metals. We also demonstrate that the presence of organic molecular fragments left from the thermal decomposition of the original molecule is critical to such stability.

PREPARATION OF FILMS

The synthesis of the coordination compound tetraneopentyl-Ti, Ti(CH_2CH(CH_3)_2)_4, represented as Ti(tetrapeptide), has already been reported.

A schematic diagram of the apparatus used for low-temperature MOCVD of tetraneopentyl-Ti is given in Fig. 1. Borosilicate glass slides, copper TEM grids, and KBr single-crystal substrates were inserted into the reaction chamber, region IV, heated in a furnace F. The temperature of the reaction zone was determined by thermocouple ThII, and the pressure, kept below 10^-3 Pa at all times, was monitored by a cold-cathode

![Fig. 1. Schematic drawing of the low-temperature organometallic MOCVD apparatus.](image-url)
XRD Spectra of TiC

![Graph showing XRD Spectra of TiC](image)

Fig. 2. XRD curves of amorphous TiC films deposited at (A) 200°C and (B) 300°C.

gage G.* The extremely air-sensitive compound was kept at 1 to 0.1 Pa in vessel I at dry ice temperature before it was placed in the reactor.

In a typical deposition run, the organometallic compound was initially introduced into zone II of the apparatus, which was cooled down to dry-ice temperatures (cold stage not shown in Fig. 1) to prevent any premature sublimation or decomposition of the compound. A first sublimation to zone III, kept similarly at dry-ice temperature, was conducted up to 40°C and 10⁻³ Pa. The residue of this initial sublimation was collected in vessel I and sealed off at S.

Furnace F was then activated and the substrates heated to the decomposition temperature of the organometallic molecule, typically 200° to 300°C. Once the substrate temperature was stabilized, a second sublimation carried the compound from zone III into the reaction chamber where it decomposed. By-products of the reaction were collected in a cold trap at liquid nitrogen temperature.

METHODS OF CHARACTERIZATION

The characterization techniques used to analyze the films included Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and electron energy loss spectroscopy (EELS). Auger spectra were recorded on a system¹ evacuated to below 10⁻¹² Pa. The analyzer transmission and resolution were 10% and ≈0.6%, respectively, for all data. A beam energy of 3 KeV was used with a beam current of 3 μA, adjusted to provide convenient measurement conditions, but kept low enough to avoid specimen damage.²⁰

In XPS analysis, the spectra, induced by MgKα radiation (1253.6 eV), were measured using an ESCA/Auger system.¹ The instrument was operated under UHV conditions (≈10⁻¹² Pa). The gold Kα line at 83.8 eV was taken as a reference line,¹⁰ and the apparatus was calibrated accordingly before every data acquisition. All survey spectra, including the narrow scans of strong lines, which were in most cases wide enough to encompass the peaks of interest here, were obtained with a pass energy of 15 eV and an energy resolution of 5% full-width at half-maximum. An X-ray source of 15 kV, 300 W was employed.²⁰

Compilation of EELS spectra was performed at 250 KeV incident electron energy in a transmission electron microscope² combined with a magnetic-sector spectrometer³ capable of 1 eV resolution attainable at any collection angle and coupled to an EDAX SW 9100/60 multichannel analyzer. The relatively high accelerating voltage has the advantage of permitting EELS analysis of thicker samples than would be possible at 100 KeV.²¹ Multiple sweeps of each spectrum were added together to give a total dwell time of ≈3 s per 1 eV channel. A beam current of ≈1 μA was focused on a 2-μm-diameter probe.

RESULTS AND DISCUSSION

FILM MORPHOLOGY

The films were of uniform thickness, continuous, silver-colored, mirror-bright, and adherent. The film thickness, determined by profiling on an alpha-step analyzer**, (2 × 10⁻³ μm resolution), was 2 μm. The films were cohesive and were recovered intact after dissolution of the Pyrex substrate in hydrofluoric acid.

The XRD scans showed that, in the 15° to 40° (2θ) region, the films obtained in the temperature range 150° to 350°C have only one very broad peak, characteristic of amorphous structures. This behavior is shown in Fig. 2 for the 200° and 300°C deposition temperatures.

Figure 3 shows the electron diffraction patterns of the same deposits, obtained by TEM. The micrographs show a few very diffuse rings, which is an additional indication of the amorphylicity of the films. The corresponding bright-field image was uniform and featureless, with no grains or microcrystallites detected.

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*Kenney Gauge, CVC Products, Rochester, NY.
¹IE 595, Physical Electronics Div., Eden Prairie, MN.
²IE 548, Physical Electronics Div.
³EM430, Philips Electronics Instruments Inc., Walhamp, MA.
⁴Model 307, Gatan Inc., Warrenville, CA.
**Tencor Instruments, Mountain View, CA.
***EM400 TEM and PW/6000D sample holder, Philips Electronics Instruments.

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Fig. 3. Electron diffraction patterns of TiC coatings produced by organometallic MOCVD at (A) 200°C and (B) 300°C.
CRystallization Temperature

Controlled heating experiments were conducted to determine the crystallization temperature of all amorphous films made. Alternate heating and examination by electron diffraction were conducted on a TEM equipped with a hot-stage sample holder capable of heating specimens to a maximum temperature of 800°C. The diffraction patterns displayed the same diffuse, broad halos characteristic of amorphous materials, Fig. 3, even at 800°C. The corresponding bright-field micrographs still showed very smooth, featureless images, indicating that no crystallites were forming. This observation implies that the crystallization temperature is >800°C for the amorphous specimens obtained.

Next, various amorphous titanium carbide samples were annealed in the TEM under the electron beam. Continuous observation and imaging in the various TEM modes were performed to reveal any structural changes occurring in the temperature range 800°C to 1400°C. Annealing was performed in a stepwise manner at 50°C intervals with 30 min at each temperature, ending at 1400°C for 2 h.

No changes were observed in the amorphous phase until 1100°C was reached. Then the amorphous-to-crystalline transition started to occur with the appearance of crystallized grains. Figure 4(A) shows the transition zone structure, displaying areas of extremely fine microcrystallites, 0.1 to 1 nm in size.

The selected-area diffraction pattern (SADP) revealed a sharp halo corresponding to the formation of a polycrystalline network (Fig. 4(B)). The network mesh size increased as the temperature was gradually raised to 1400°C. Grain growth to 4 to 5 nm was observed, as can be seen from the bright-field image in Fig. 5(A). Individually resolvable spots were detected in SADP, superimposed on the sharp ring pattern (Fig. 5(B)).

Thus, from in-situ TEM annealing, one can conclude that the crystallization of amorphous TiC films begins to occur at ~1100°C.

Effects of Growth Conditions

The conditions for thermal decomposition of tetranoxytitanum were investigated as a function of temperature, pressure, and the nature and shape of substrates. It was found that the deposition process is strongly affected by the gas pressure and reaction temperature.

Figure 6 shows the relation between the growth rate of TiC films on glass borosilicate microslides and substrate temperature at fixed pressure (~10^-7 Pa) and consequently constant gas flow rates. The growth rate is apparently zero at temperatures <125°C. The formation of titanium carbide is initiated rapidly at 150°C, above which the deposition rate increases progressively with increasing temperature. A film ~2 μm thick was obtained at a substrate temperature of 300°C. It can be seen from Fig. 6 that a suitable temperature for amorphous TiC film deposition is 250°C—the threshold for optimum growth rate of the amorphous phase.
The influence of pressure, and therefore gas flow rate, on the decomposition mechanism of tetraneopentyl-titanium is illustrated in Fig. 7 for a constant temperature of 300°C. Amorphous titanium carbide films were found to be deposited below $10^{-2}$ Pa, although the reaction yield was extremely low under $10^{-4}$ Pa. On the other hand, small TiC crystallites started to grow above $10^{-2}$ Pa. The corresponding electron diffraction micrographs display sharp, well-defined rings, located at the appropriate d-spacing for crystalline TiC (see Fig. 4(B)). A suitable pressure range for deposition of amorphous TiC coatings seems to be $10^{-4}$ to $10^{-2}$ Pa.

We identified the following two mechanisms as probable causes for the observed amorphous to crystalline transition associated with the increase in gas pressure.

(1) At the higher gas pressure ($>10^{-2}$ Pa) the mean-free-path for tetraneopentyl-titanium molecules in the gas phase is less than the dimensions of the reactor (short mean-free-path), thus leading to an increased probability for collisions with the reactor walls and with the other molecules. Consequently, when the molecules, sublimed at very low temperatures ($<250°C$), reach the relatively hot reaction zone (200° to 350°C) and thermolyze, the high collision probability might lead to their dissociation into smaller fragments —new titanium species with reduced hydrocarbon contents—that would be possible at low pressures ($<10^{-3}$ Pa). Hence, the developing film has less chance of trapping the large organic fragments associated with the stability of the amorphous phase. The inclusion of hydrogen is equally improbable and the latter is expected to be eliminated as H$_2$ or as some light hydrocarbon molecule in the vacuum system.

(2) A second possibility is that the thermolysis products reach the substrate with higher kinetic energies. Hence, more energy would be delivered locally to the surface where it could be utilized to allow migration (atomic rearrangements) to the crystalline configuration and ejection of the volatile hydrocarbon fragments that were formed.

To test these hypotheses, analysis of the gas in the reaction chamber and of the gaseous by-products with a quadrupole mass spectrometer residual gas analyzer is planned. By contrast, at low enough pressures, the molecular mean-free-path is limited only by the chamber walls (long mean-free-path), and dissociation into smaller molecular fragments during the thermal decomposition is highly improbable. Consequently, small concentrations of hydrogen are expected to be included in the coatings in organic clusters and trapped gases. These inclusions probably severely retard atomic migration and hence inhibit nucleation and growth of crystallites.

$$\text{Ti(neopentyl)}_4 \quad P > 10^{-2} \text{ Pa} \rightarrow \text{TiC}_{\text{cryst}}$$
$$P < 10^{-2} \text{ Pa} \rightarrow \text{TiC(H)}_{\text{amorphous}}$$

Further studies (X-ray photoelectron spectroscopy, XPS etc.) were done to confirm these expectations (see section "XPS analysis").

Deposition onto substrates other than borosilicate glass, mainly KBr crystals and copper, was also examined. The deposition rates on copper and KBr crystals were found to be higher than on borosilicate glass slides. This difference might be due to the higher thermal conductivity of the substrates rather than to their chemical nature. The adherence of the deposits to borosilicate glass...
Fig. 10. Energy-loss spectrum of amorphous TiC films, showing C-K, Ti-L_{2,3}, and L_{1} edges.

and Cu substrates was greater than to KBr, where they were often found to peel off.

AES RESULTS

Auger electron spectroscopy of the MOCVD deposited TiC films after extensive sputtering of the films' surfaces gave signals for titanium and carbon with oxygen signal near the AES detection limits (Fig. 8(A)). The carbon signature in films obtained below $10^{-3} \text{ Pa}$ is similar to that for uncombined carbon rather than crystalline TiC (Fig. 8(B)) and suggests that either free carbon is present in the films, or that combined carbon in amorphous TiC has an electronic environment markedly different from that in crystalline TiC. Since no carbon particles were seen in XRD and SADP, the latter interpretation is favored. By contrast, the carbon signature for TiC coatings obtained at pressures above $10^{-1} \text{ Pa}$ is similar to that for TiC crystals (Fig. 9(C)), which indicates that the local chemical environment of C atoms in both cases is the same.

Figure 9 shows the relative C, Ti, and O signals corresponding to an atomic concentration depth profile. The results indicate a high oxygen content near the films' surfaces that falls off to a negligible amount in the film. The corresponding atomic composition, 50.7% Ti, 47.3% C, and <2% O, gives a carbon/metal ratio $x = 0.93$.

EELS STUDIES

The EELS spectra were collected with a rather broad incident electron beam (2 μm in diameter) thus allowing for an optimization of the elemental sensitivity and a reduction in radiation and thermal effects. A liquid-nitrogen-cooled TEM side-entry specimen stage was also used for cooling the samples to $-178^\circ \text{C}$, thereby diminishing mass loss and thermal effects.

Energy-loss spectra of our TiC films showing C-K and Ti-L_{2,3} and L_{1} edges are displayed in Fig. 10. The results confirm our earlier predictions from Auger spectroscopy, in particular the absence of oxygen in the deposits.

XPS ANALYSIS

Binding energies of core electrons for elements in titanium carbide films obtained by MOCVD of tetraneopentyl-Ti at two different pressures, $5 \times 10^{-3} \text{ Pa}$ and $10^{-1} \text{ Pa}$, were measured using XPS.

For the films deposited at $5 \times 10^{-3} \text{ Pa}$, a Ti2p_{3/2} peak at 458.8 eV (Fig. 11(A)) was detected at the film surface and is attributed to TiO_{2}. The broadness of the Ti2p_{3/2} peak, as seen in Fig. 11(B), and its shift to lower binding energies during sputtering of the film surface layers, indicate the presence of a mixture of two phases, most probably TiC and TiO_{2}, in the films and a gradual decrease in the degree of oxidation. The Ti2p_{3/2} peak was observed to shift to much lower binding energy, 455.1 eV, after extensive sputtering yielded complete removal of surface contamination (Fig. 11(C)). This energy is assigned to the presence of titanium carbide in the films. Negligible oxygen concentrations were recorded at this depth ($\approx 15$ to 20 nm below the film surface), which, within the detection limits, is in agreement with our earlier results from AES and EELS. The CsIs spectrum from the surface (Fig. 12(A)) exhibits one peak at 284.6 eV. This value is associated with hydrocarbon, C-C, and C-H bonds. A second peak at 281.6 eV, attributed to carbon in titanium carbide, started to appear during removal of surface layers. Upon complete removal of the surface layer by argon bombardment, two CsIs levels were observed, one at 281.6 eV and the other, much broader and of lower intensity, at 284.4 eV (Fig. 12(C)). The former is attributed to titanium carbide, whereas the latter is close to the value found by Johansson et al. We assign it to hydrogenated carbon. This peak indicates that organic molecules are indeed present in the coatings.
CONCLUSIONS

Low-temperature (200° to 300°C) and low-pressure (<10⁻⁴ Pa) MOCVD of tetraoctyl-Ti gave amorphous titanium carbide films with 50.7 at% Ti and 47.3 at% C, for a carbon-to-metal ratio of -0.93. These films were stable against crystallization to an appreciably higher temperature, 1100°C, than typical glassy metals. This outstanding stability is believed to be closely related to the presence of organic molecular fragments and hydrocarbon clusters in the films. These entities probably reduce molecular migration for Ti and C and hence limit the process of nucleation and growth of crystallites.

An amorphous-to-crystalline transition was observed (for decomposition temperatures in the range 220° to 350°C) when the pressure in the MOCVD reactor was increased above 10⁻² Pa. It was suggested that this structural change was probably due to variations of the molecular mean-free-path in the gas phase with pressure. At high enough pressures (10⁻² Pa) the smaller hydrocarbon byproducts of the thermolysis have less probability of being trapped in the films and therefore less chance to stabilize the amorphous phase. The absence of these fragments in the XPS spectra of the TiC (crystalline) coatings prepared above 10⁻² Pa seems to confirm this hypothesis. Another possibility is that, above 10⁻² Pa, the thermolysis products impinged on the substrate with higher kinetic energies and thus were allowed more freedom to migrate to the crystalline configuration.

The amorphous TiC films deposited on borosilicate glass substrates were of uniform thickness, continuous, silver-colored, mirror-bright, and adherent, with an average thickness of 2 μm. Their thickness can be tailored by varying the deposition temperature, pressure, and duration of the reaction. The films displayed strong adhesion to the glass substrate and retained their integrity after dissolution of the substrate in hydrofluoric acid.

The low temperatures (~200° to 300°C) characteristic of this MOCVD process may make possible the deposition of TiC films on substrates such as polymers that would pyrolyze and metals that would melt at the usual TiC/CVD temperatures of 1200° to 1350°C.

ACKNOWLEDGMENTS

We thank Alex Green, John Woodhouse, Nancy Finnegan, and Carol Kozlowski for instruction in the techniques applied. We also extend our appreciation to the staff of the Coordinated Science Laboratory glass shop and the Materials Research Laboratory machine shop, in particular Bill Lawrence, Bud Dittman, and Pat Watson for their invaluable expertise. We acknowledge the assistance of JoAnn Brennan and express our gratitude for her extreme patience. We also thank James A. Jensen for his invaluable help in
the preparation of the organometallic compound used. Clare M. Allocco thanks the SOHIO Engineered Materials Co. for fellowship support.

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