



## INTRINSIC STRESS AND HIGH TEMPERATURE PROPERTIES OF METAL-CONTAINING HYDROGENATED AMORPHOUS CARBON COATINGS

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### ABSTRACT

*Metal-containing hydrogenated carbon (Me-C:H) coatings have been studied for a few decades and proved to have extensive applications. As members of the Me-C:H family, Ti-containing hydrogenated carbon (Ti-C:H) and W-C:H coatings have been developed typically for mechanical purposes. However, their applications are constrained by the presence of large residual stresses within the coating and degradation at high temperature. Both issues are addressed in this presentation.*

A detailed examination of the intrinsic stress development within and mechanical properties of Ti-C:H and W-C:H coatings deposited in an inductively coupled plasma (ICP) assisted hybrid chemical vapor deposition (CVD)/physical vapor deposition (PVD) environment was carried out [1, 2], combining in-situ substrate curvature measurements with plasma probe measurements, ex-situ electrical resistivity measurements, and instrumented nanoindentation measurements. Intrinsic stresses within Ti-C:H and W-C:H were found to be compressive over wide ranging compositions and plasma parameters. The intrinsic compression within Ti-C:H was found to depend significantly on the Ti composition (Fig. 1), and was related to a percolation type transition in the nanoscale structure. The intrinsic compression within Ti-C:H was further shown to be significantly influenced by the energy of ionic species bombarding the substrate during growth (Fig. 2). Measured stress – thickness history was discussed in terms of possible mechanisms contributing to intrinsic stress generation. Although there are likely multiple mechanisms influencing intrinsic stress development, our present results suggested that ion bombardment played a significant role in intrinsic stress generation within Ti-C:H, and was likely to influence stress development in other low temperature deposited amorphous hydrocarbon based ceramic nanocomposite coatings.

Structural and mechanical characterization was performed on Ti-C:H specimens deposited at  $\sim 600^\circ\text{C}$  by combining the techniques of X-ray photoelectron

spectroscopy, electron diffraction and transmission electron microscopy, instrumented nanoindentation, X-ray absorption spectroscopy, and Raman scattering spectroscopy [3]. The structural and mechanical characteristics of these specimens were compared to those deposited at the lower temperature of  $\sim 250^\circ\text{C}$ . The results indicated that Ti-C:H consisted of a nanocrystalline TiC phase and an hydrogenated amorphous carbon (a-C:H) phase, and that Ti atoms were incorporated into Ti-C:H predominantly as B1-TiC. Deposition at  $\sim 600^\circ\text{C}$  promoted TiC precipitation, resulting in little Ti dissolution within the a-C:H matrix. High temperature deposited Ti-C:H specimens were found to possess lower modulus and hardness values as compared to low temperature deposited specimens, especially at low Ti compositions. This was rationalized by electron microscopy evidence of increased short and medium range graphitic order within the a-C:H matrix of high temperature deposited Ti-C:H, and supported by additional Raman spectroscopic observations (Fig.3). Annealing treatment at  $600^\circ\text{C}$  combined with Raman scattering measurements showed that the a-C:H matrix in high temperature deposited Ti-C:H specimens appears to be less structurally sensitive to additional high temperature annealing.

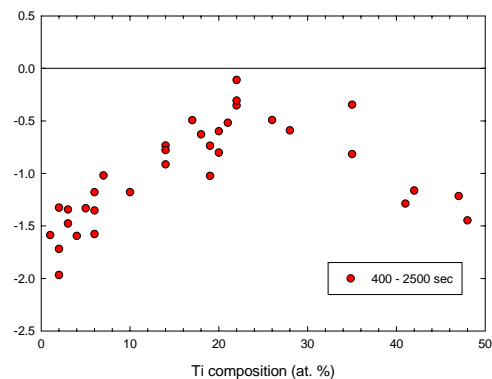


Fig. 1 Average intrinsic stress during late stage Ti-C:H growth as a function of the Ti composition.

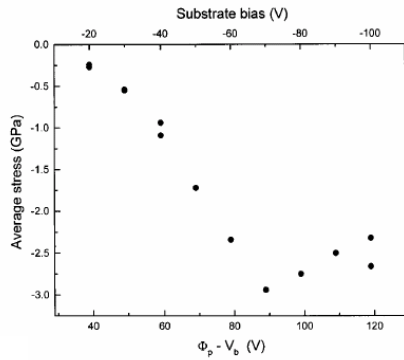


Fig. 2 Late stage average intrinsic stress within Ti-C:H as a function of the ion energy.

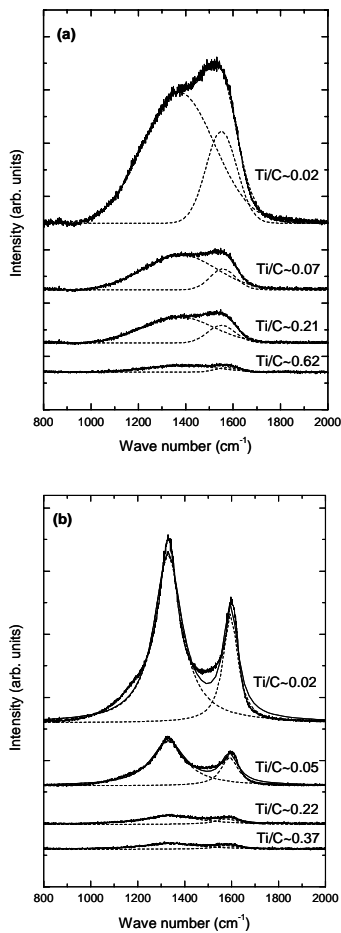


Fig. 3 Raman scattering examination of as-deposited Ti-C:H specimens deposited at  $\sim 250^\circ\text{C}$  (a) and  $\sim 600^\circ\text{C}$  (b).

The effective coefficients of thermal expansion (CTE) of Ti-C:H coatings with compositions ranging from nearly pure a-C:H to nearly pure TiC were measured [4]. Effective CTEs were determined from temperature induced changes in the curvature of film/substrate assemblies, measured with a multi beam optical sensing technique. Measured effective

CTE values for Ti-C:H are consistent with previous measurements on a-C:H thin films, and show little dependence on the Ti composition, and is  $\sim 5.7 \times 10^{-6} \text{K}^{-1}$ .

Highly hydrogenated carbon films, with hydrogen content approaching 60 at.%, were deposited with a modified ICP assisted CVD technique. Flux of gas-phase ionic species to the substrate surface was greatly reduced by inserting a glass tube-grounded wire-mesh screen assembly between a CH<sub>4</sub>/Ar inductively coupled plasma and the Si substrate. Characterization of films deposited by conventional and modified ICP assisted CVD was accomplished by combining the techniques of hydrogen elastic recoil detection (Fig. 4), Raman scattering spectroscopy, and instrumented nanoindentation. Film thermal stability was studied through high temperature annealing in vacuum. It was suggested that a decreased ratio of ionic species flux to activated neutral species flux at the substrate during deposition is responsible for the increased hydrogen incorporation into the film.

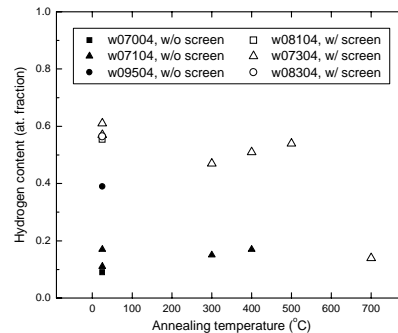


Fig. 4 Hydrogen composition as a function of annealing temperature for a 450nm thick hydrogenated carbon film deposited in the modified mode and a 300nm thick hydrogenated carbon film deposited in the conventional mode. Hydrogen contents of several other films in the as-deposited state, deposited in the modified and conventional modes, are also shown. Identical symbols at the same temperature denote results of repeat measurements.

## ACKNOWLEDGMENTS

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