LETTER TO THE EDITOR

Journal of Non-Crystalline Solids 442 (2016) 40–43

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

A scanning electron microscopy and energy dispersive X-ray spectroscopy analysis of the substrate-to-thin-film-surface cross-section of thin carbon films deposited on curved Ti_6Al_4V substrates with and without silicon adhesion layers

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ARTICLE INFO

Article history:
Received 20 January 2016
Accepted 23 February 2016
Available online 10 April 2016

Keywords:
Thin-film carbon
Silicon interlayer
Adhesion
Curved Ti_6Al_4V substrates
Scanning electron microscopy
Energy dispersive X-ray spectroscopy.

ABSTRACT

Thin-film carbon is deposited onto curved Ti_6Al_4V substrates with and without silicon interlayers through the use of an economical plasma enhanced chemical vapor deposition process. Through the use of scanning electron microscopy coupled with energy dispersive X-ray spectroscopy, visualizations of the substrate-to-thin-film-carbon-surface cross-sections are acquired. Basic adhesion tests on the resultant thin-film/substrate systems are performed. It is shown that a silicon interlayer dramatically enhances the adhesion of thin-film carbon onto the underlying substrate. A means of characterizing the EDX signal transitions, between the various regions in these cross-sections, is devised and employed in the analysis of these thin-film/substrate systems.

1. Introduction

Thin-films of carbon are now finding applications in a wide variety of industrial and commercial settings [1]. In the preparation of thin-film carbon, it is often the case that an intermediate layer of thin-film foreign material is coated onto the underlying substrate first, prior to the deposition of the thin-film of carbon itself [2,3,4]. Research has demonstrated that this coating layer, present between the underlying substrate and the thin-film of carbon, dramatically increases the adhesion of the thin-film carbon onto the underlying coated substrate [2,5–8]. These coatings of foreign materials are often just referred to as adhesion layers or interlayers.

While visualizations of the surface of thin-films of carbon have been acquired [5,7,9], true cross-sectional analyzes, from the underlying substrate to the surface of the thin-film carbon, have yet to be reported. In this brief letter, we employ scanning electron microscopy (SEM), coupled with energy dispersive X-ray spectroscopy (EDX), in order to critically contrast the cross-section obtained for a thin-film of carbon deposited onto a silicon coated substrate, where silicon serves as the interlayer, with that corresponding to a thin-film of carbon deposited directly onto the underlying substrate, i.e., without an interlayer. The novelty in this analysis primarily rests in our use of the conjuncture of these two experimental approaches, i.e., SEM and EDX, in the study of the substrate-to-thin-film-carbon-surface cross-section, with and without an interlayer [10].[1] The benchmarking of our obtained results, which correspond to thin-films of carbon deposited through very economical means, i.e., without the use of a turbo pump, with those prepared using more conventional approaches, is an additional novel contribution of this analysis. Finally, a means of characterizing the transitions in the EDX signals, between the various regions in these cross-sections, is devised and employed in the analysis of these thin-film/substrate systems.

This paper is organized in the following manner. In Section 2, the preparation of the samples and the experimental procedures followed in this analysis are described. The results, corresponding to these cross-sectional analyzes, are then presented in Section 3. Finally, some conclusions are offered in Section 4.

2. Experiment

Two samples of thin-film carbon are prepared through the use of plasma enhanced chemical vapor deposition (PECVD). A small and

[1] It should be noted, however, that Sakamoto et al. [10] performed an analysis of the substrate-to-thin-film interface for thin carbon films deposited directly onto silicon substrates without an interlayer. Our analysis is distinct from that of Sakamoto et al. [10] in the sense that here we examine the entire cross-section, from the substrate to the thin-film carbon surface, and we contrast the cross-section obtained with and without an interlayer.

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http://dx.doi.org/10.1016/j.jnoncrysol.2016.02.017
0022-3093/

economical deposition system is used for the purposes of these depositions. No expensive pumping equipment, i.e., turbo pump, is employed for these depositions. One of the samples, hereafter referred to as Sample 1, is prepared without an interlayer, while the other sample, hereafter referred to as Sample 2, is prepared through the use of a silicon interlayer. The thin carbon films are produced through the use of hexane gas and the silicon interlayer is produced through the use of tetramethylsilane (TMS) gas. Two reference samples are used in order to provide benchmark results for our study. One of the benchmark samples, Sample 3, is deposited through the use of conventional rf magnetron sputtering directly onto the underlying substrate, without the use of a silicon interlayer; a turbo pump is employed for this deposition [11]. The other benchmark sample, hereafter referred to as Sample 4, is prepared using a conventional PECVD deposition approach, i.e., using a turbo pump, methane gas being employed in order to produce the thin-film of carbon and silane gas being used in order to produce the silicon interlayer [2].

The substrates employed for this experiment, an alloy of titanium, aluminum, and vanadium (Ti_6Al_4V), are commonly found in industrial applications, and have already been the subject of multiple studies [2,7,8,12,13]. Curved substrates, i.e., rings, are employed for the purposes of this analysis, as the adhesion directly onto a curved Ti_6Al_4V substrate is found to be considerably greater than that onto a corresponding flat substrate; the reasons for this remain unknown at present. The radius of curvature of the substrates is around 10 mm for all of the samples considered in this analysis.

The substrates used for Samples 1 and 2 are polished and then cleaned for 20 min in an ultrasonic bath with 5% all-purpose cleaner (TSP) in tap water and also for 2 min in an ultrasonic bath with pure acetone prior to deposition. An argon plasma cleaning step, performed prior to deposition, is performed with a gas flow of 20 sccm at 170 mTorr. The base pressure employed for these depositions is 36 mTorr. The pressure during the carbon thin-film deposition itself, i.e., the deposition pressure, is held at 400 mTorr. During the silicon interlayer deposition, the deposition pressure is held at 300 mTorr. The TMS gas used to produce the silicon interlayer, being in possession of an abundance of carbon and silicon atoms, introduces a transition layer, between the silicon interlayer and the thin-film of carbon; the silicon interlayer itself is expected to have a significant carbon content as well, owing to the presence of carbon atoms within TMS gas. Samples 3 and 4 are deposited with deposition pressures of about 50 and 80 mTorr, respectively; turbo pumps are used for the depositions of both Samples 3 and 4, the base pressure being around 10^{-6} Torr for both cases.

Following deposition, each sample is characterized through the use of SEM and EDX across the cross-section, i.e., from the underlying substrate to the surface of the thin-film of carbon. The interfaces between the different layers are rendered visible through polishing the sides of the samples, first with a silicon carbide sandpaper (320 grit) and then with a 3 μm diamond slurry. A Scotch tape test, a widely used test for low adhesion thin-films, is applied to the samples considered in this work [5,14–17]. The results of this test are depicted in Table 1. The results clearly demonstrate increased adhesion owing to the presence of the silicon interlayer.

Table 1
An overview of the adhesion tape tests.

Substrate	Deposition process	Interlayer	Result
Sample 1	PECVD	No interlayer	Well adhering, no removal with Scotch tape test
Sample 2	PECVD	TMS interlayer	Very well adhering, no removal with Scotch tape test
Sample 3	Sputtering	No interlayer	Well adhering, only small parts peeled off with Scotch tape test
Sample 4	PECVD	Silane interlayer	Very well adhering, no removal with Scotch tape test

3. Results and discussion

SEM and EDX cross-sectional scans, corresponding Samples 1, 2, 3, and 4, are shown in Figs. 1, 2, 3, and 4, respectively. Transitions, between the different regions in these cross-sections, are clearly in evidence. In the SEM images, these transitions correspond to changes in the texture and shading of the observed image. For the corresponding EDX results, however, changes in the chemical composition are interpreted as being related to transitions between the different regions in the cross-section. Some have interpreted the EDX signal as providing a virtually direct measure of the distribution of the elemental species across such a cross-section; see, for example, Sakamoto et al. [10]. We believe, however, that this is an overly broad inference, as the EDX probing beam probes a volume rather than a point. Thus, EDX signals, even for the case of the most sharp material transitions, do not exhibit abrupt transitions in of themselves. Instead, the volume averaging that occurs leads to a smearing in the results over the transitions, i.e., there is an encroachment from the neighboring regions.

We believe that meaningful insights into these thin-film/substrate systems may be gleaned through a systematic analysis of the form of these EDX signals across the transitions between the different regions in these cross-sections. In particular, plotting these EDX signals on a logarithmic scale, an EDX signal encroachment depth, δ, corresponding to the reciprocal of the exponential extinction coefficient, may be determined. We distinguish between two types of encroachment depths, one corresponding to the EDX signal transition from the substrate-to-the-thin-film, the other corresponding to the EDX signal transition from the thin-film-to-the-substrate; by thin-film, we are referring to both the interlayer and the thin-film of carbon in the event that an interlayer is being employed. For the substrate-to-thin-film encroachment depth evaluations, we focus on the Ti signal for all cases. In contrast, for the thin-film-to-substrate encroachment depth evaluations, we focus on the C signal for all cases.

The EDX signal encroachment depth evaluations found for our analysis are presented in Table 2. For the substrate-to-thin-film EDX signal transition, the encroachment depths corresponding to Samples 1 and 2 are found to be larger than those associated with Samples 3 and 4; see Fig. 5. It is noted that the deposition pressures associated with Samples 1 and 2 are greater than those associated with Samples 3 and 4. Hsu et al. [18] and Grill et al. [19] provide evidence that suggests that a lowering of the deposition pressure will lead to an increase in the thin-film density. It seems plausible that the EDX signal encroachment depth is inversely proportional to the material density, i.e., the greater the mass density, the less the EDX signal encroachment depth, δ. Accordingly, the observed results seem to make intuitive sense [20].

The thin-film-to-substrate EDX signal transitions are found to be considerably sharper than their corresponding substrate-to-thin-film counterparts, i.e., the corresponding EDX signal encroachment depths, δ, are found to be smaller, presumably owing to the higher density of the Ti_6Al_4V substrates compared with the thin-films of carbon. Differences in the EDX signal encroachment depths, corresponding to the thin-films deposited with and without a silicon interlayer, are also observed, the thin-films grown with an interlayer having greater EDX signal encroachment depths. This is probably owing to the smaller density of silicon compared with the thin-films of carbon [21].[2]

[2] The mass density of thin-film silicon is around 2.2 g/cm^3, while carbon thin-films have mass densities ranging between 2.4 g/cm^3 and 3.1 g/cm^3 [21].