

## ***In situ* diagnostics of film thickness and surface roughness of diamond films on a Ti–6Al–4V alloy by optical pyrometry**

Shane A. Catledge, Walton Comer, and Yogesh K. Vohra<sup>a)</sup>

*Physics Department, University of Alabama at Birmingham (UAB), Birmingham, Alabama 35294-1170*

(Received 25 March 1998; accepted for publication 11 May 1998)

The thickness and surface roughness of diamond films grown on a Ti–6Al–4V alloy in a microwave plasma reactor was measured *in situ* using optical pyrometry. The growing film results in oscillations of the apparent temperature with time, which can be explained by interference effects caused by reflections from the film/air and film/substrate interfaces. The equation governing the transmittance of the diamond/metal system has been derived by taking into account the complex index of refraction of an absorbing substrate. The apparent temperature was modeled using this relation for the transmittance in order to extract the time dependence of film thickness, surface roughness, and the true temperature of the substrate. The growth rate was observed to exhibit two regimes: an initial period of slowly increasing growth followed by a growth rate that was about 50% higher. The surface roughness increased at a nearly uniform rate but quickly reached a saturation roughness for long deposition times (high surface roughness). The limitation of the model for films in the high surface roughness regime is discussed. © 1998 American Institute of Physics. [S0003-6951(98)03428-7]

*In situ* growth rate measurements during molecular beam epitaxy using an optical pyrometer were first carried out by SpringThorpe *et al.*<sup>1</sup> The application of this technique has been extended to diamond films during plasma assisted chemical vapor deposition (CVD).<sup>2,3</sup> This technique has been used to investigate the effects of different feed gas mixtures on diamond nucleation, growth rate, and surface roughness.<sup>4</sup> The growing film results in oscillations of the apparent temperature  $T_{\text{app}}$  with time, which can be explained by interference effects caused by reflections from the film/air and film/substrate interfaces. The periodicity and decay of the envelope of the oscillations allows for measurement of the instantaneous growth rate and surface roughness. However, the model which has been developed<sup>5</sup> to extract these film properties does not fully account for the case of an absorbing substrate in which the complex index of refraction must be used. We report here a revised expression for the transmittance of the film grown on an absorbing substrate and use this to model  $T_{\text{app}}$  for diamond films grown on Ti–6Al–4V alloy substrates (90% Ti, 6% Al, and 4% V by weight). The corresponding film thickness  $d$  and surface roughness  $\sigma$  were obtained as a function of deposition time. In addition, the more general case of a pyrometer situated at a nonzero angle relative to the substrate normal is included in the model.

The diamond films were deposited on 7 mm diam polished Ti–6Al–4V substrates in a 1.2 kW microwave plasma reactor. The initial surface roughness of the substrates as measured by profilometry was between 12 and 18 nm. The deposition conditions and measured properties of the films are listed in Table I. The pyrometer was located 20 in. from the substrate at an angle of 55° from the substrate normal (wavelength centered at 1.6  $\mu\text{m}$ ). The CH<sub>4</sub>/H<sub>2</sub> plasma is essentially transparent at the pyrometer wavelengths.

A schematic showing the substrate/film system and pyrometer geometry is shown in Fig. 1. Unpolarized light emitted from the substrate during deposition is transmitted through the nonabsorbing diamond film. A portion of the light (approximately 37% in this geometry) is internally reflected and undergoes successive reflections within the film, transmitting 63% at each diamond/air interface. The pyrometer is situated at an angle of 55° with respect to the substrate normal and so only light exiting the film at this angle is considered. In general, for non-normal incidence angles, the state of light polarization must be considered when calculating the Fresnel reflection coefficients. For the geometry of Fig. 1 the angle of incidence  $\theta$  for light transmitting through the diamond/air interface is 20.1°. This angle is very close to Brewster's angle,  $\theta_b = \tan^{-1}(1/n) = 22.8^\circ$ , at which the reflected light is completely polarized with its *E*-field vibrating parallel to the plane of the film surface (TE mode). Therefore, the transmitted light is partially polarized with a preferred *E*-field vibration perpendicular to the plane of the film surface (TM mode). In calculating all Fresnel reflection coefficients the TE mode has been assumed.

The equation for the apparent temperature in terms of the true film/substrate temperature  $T$  and the transmittance of the film  $\mathcal{T}_{\text{film}}$  is<sup>5</sup>

$$T_{\text{app}} = \frac{T}{1 - (T/T_o) \ln[\mathcal{T}_{\text{film}}(\lambda, d, \sigma) / \epsilon(\lambda, T)]}, \quad (1)$$

where  $\epsilon(\lambda, T) = 0.4$  is the emissivity of the titanium substrate and  $T_o = hc/k_B\lambda = 9014$  K for  $\lambda = 1.6$   $\mu\text{m}$ . The equation governing the transmittance of the film has been previously presented for the case where absorption by the substrate can be neglected (such as for silicon where  $k = 0$  in the infrared region). We now show how the equation for the film transmittance must change when considering absorbing substrates in which the index of refraction is complex (i.e.,  $k \neq 0$ ). In following with a similar procedure for determining the trans-

<sup>a)</sup>Electronic mail: vohra@phy.uab.edu

TABLE I. Deposition conditions and measured properties for diamond films on Ti-6Al-4V substrates.

Film	CH <sub>4</sub> /H <sub>2</sub> flow rates (sccm)	Chamber pressure and microwave power	Substrate temperature (°C)	Total deposition time (h)	Final thickness, <i>d</i> (modeled) <i>d</i> (measured) (μm)	Avg. growth rate 1st 3 h: Remainder (μm/h)	Final roughness, <i>σ</i> (modeled) <i>σ</i> (measured) (μm)
1	5/495	80 Torr 750 W	730 ± 10	12.0	1.8 ...	0.14:0.21	0.15 ...
2	5/495	80 Torr 680 W	735 ± 15	19.5	3.8 3.8 ± 0.5	0.15:0.22	0.13 0.144 ± 0.026

mission coefficient through a nonabsorbing film with thickness  $d$  and surface roughness  $\sigma$  as outlined in Ref. 6, where now the radiation is emitted from the surface of an absorbing substrate at an angle  $\theta$ , the transmission coefficient for the system  $t_{\text{sys}}$  is

$$t_{\text{sys}} = \frac{S_t r_{10} \exp\left(-i \frac{2\pi n d \cos \theta}{\lambda}\right)}{1 - S_{\text{int}} r_{10} r_{12} \exp\left(-i \frac{4\pi n d \cos \theta}{\lambda}\right)}. \quad (2)$$

The subscripts on the Fresnel coefficients in Eq. (2) refer to the media involved (see Fig. 1) and the directions of incoming/outgoing light. The terms  $S_t$  and  $S_{\text{int}}$  account for

surface scattering of light transmitted through and internally reflected from the diamond/air interface, respectively. They are defined<sup>6</sup> as follows:

$$S_t = \exp\left\{-\frac{1}{2} \left[\frac{2\pi(n-1)\sigma}{\lambda}\right]^2\right\}$$

and

$$S_{\text{int}} = \exp\left[-\frac{1}{2} \left(\frac{4\pi n \sigma}{\lambda}\right)^2\right]. \quad (3)$$

The transmittance for the diamond/metal system is determined as  $\mathcal{T}_{\text{film}} = (t_{\text{sys}})(t_{\text{sys}}^*)$ ,

$$\mathcal{T}_{\text{film}}(\lambda, d, \sigma) = \frac{S_t^2 (1 - r_{10}^2)}{1 + (r_{10}|r_{12}|S_{\text{int}})^2 - 2r_{10}S_{\text{int}}[\text{Re}(r_{12})\cos(\delta) - \text{Im}(r_{12})\sin(\delta)]}, \quad (4)$$

where the phase factor  $\delta = 4\pi n d \cos \theta / \lambda$  and now the real and imaginary parts of the diamond/metal reflection coefficient are accounted for.

The transmittance of the diamond/metal system as expressed in Eq. (4) was used along with Eq. (1) to model  $T_{\text{app}}$  for diamond films grown on the Ti-6Al-4V alloy. During the fitting process that was used to determine film thickness  $d(t)$ , surface roughness  $\sigma(t)$ , and true substrate temperature  $T(t)$ , it was clear that the model predicted too rapid a decay of  $T_{\text{app}}$  for films grown beyond the point where the oscillations die out (i.e., large  $\sigma$ ). This limitation was explained by Akkerman *et al.*<sup>5</sup> as a result of the model incorrectly predicting the transmittance to approach zero in the limit of a very rough surface. For the fitting process, we allowed the true temperature to float under the constraint that the true temperature should approach  $T_{\text{app}}$  once the oscillations die out, as expected for a rough surface.

Figure 2 shows the observed oscillations and modeled results of  $T_{\text{app}}$  for diamond films grown for 12 h (film 1) and 19.5 h (film 2). An initial period of no diamond film growth in which the substrate surface is presumed to be undergoing carburization is shown (a TiC phase was observed in the postdeposition x-ray diffraction analysis). For purposes of the model, time  $t=0$  is designated at the beginning of the first oscillation at which point the diamond film starts to

grow. The substrate temperature for film 2 was decreasing at the time the methane was introduced causing the first oscillation to drop well below the starting substrate temperature. The oscillation amplitude in  $T_{\text{app}}$  for film 2 was almost completely damped after about 12 h of deposition. Therefore, the fitting process for  $d(t)$  beyond this time was not certain and a linear extrapolation of the film thickness was assumed.

The modeled time dependence for the film thickness and surface roughness for each film are shown in Figs. 3 and 4,

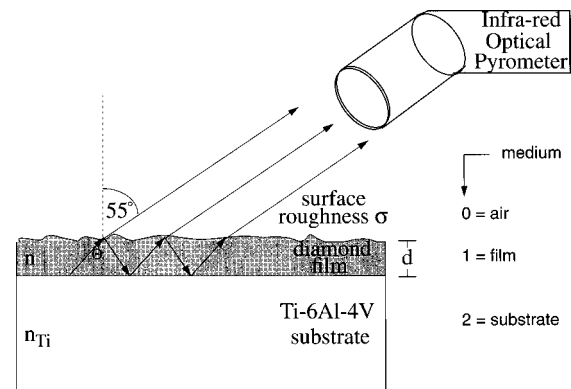


FIG. 1. Schematic of substrate/film system and pyrometer geometry. The pyrometer is located 20 in. from the substrate at an angle of 55° from the substrate normal.

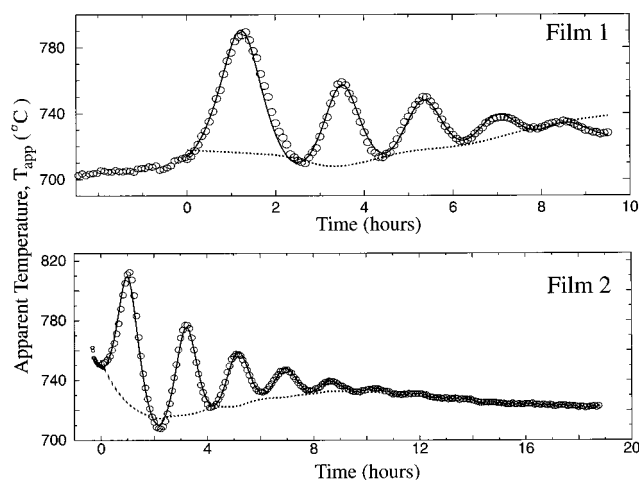


FIG. 2. The observed oscillations of  $T_{app}$  (circles) and the predictions of the model for the diamond/metal system (solid line) are shown for films 1 and 2 grown on Ti-6Al-4V substrates. The dashed line is the true substrate temperature also obtained from the model.

respectively. Each film exhibits two distinct regimes in growth rate: an initial period of slowly increasing growth ( $\sim$  first 3 h) followed by a growth rate that was about 50% higher. This change in growth rate may indicate a gradual transition between the formation of interfacial phases and the growth of diamond. It is also interesting to note that the true substrate temperature for each film shows an increase starting at about the 3 h mark. This increase in temperature may also contribute to the faster growth rate after this time.

The trends observed in the time dependence of the surface roughness as shown in Fig. 4 are more complicated. The rate of roughness increase,  $\Delta\sigma/\Delta t$ , is constant for the first 8 h of growth for film 2, but increases slightly for film 1. In addition, the final roughness for film 2 is lower than that of film 1 even though it was grown thicker. Small differences in the initial surface condition of the substrate (e.g., initial roughness, nucleation site density) or in the initial deposition conditions may explain these trends. The scatter in roughness after about 10 h for film 2 is attributed to the limitation of the model in accurately predicting the decay of  $T_{app}$  with time. A similar scatter has also been observed in modeling diamond films grown on silicon substrates.<sup>3</sup> Finally, although both

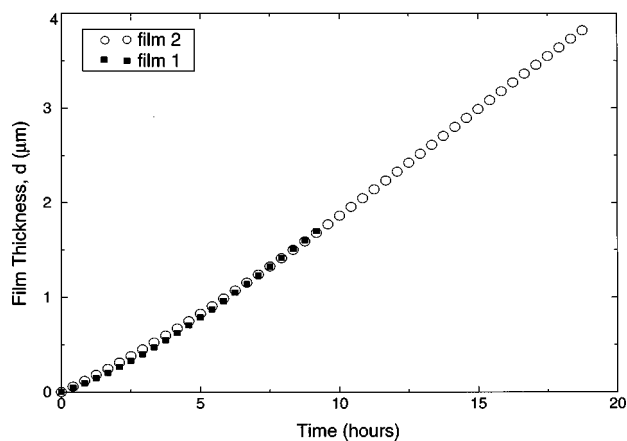


FIG. 3. The time dependence of film thickness for films 1 and 2 as predicted from the model. Two distinct growth regimes are identified from the slopes, suggesting a change in the growth kinetics.

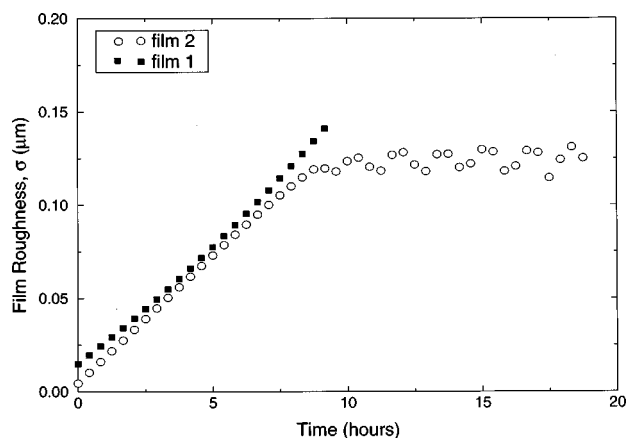


FIG. 4. The time dependence of surface roughness for films 1 and 2 as predicted from the model. The scatter in roughness after about 10 h for film 2 is attributed to the limitation of the model in accurately predicting the decay of  $T_{app}$  with time.

films in this study delaminated upon cooling to room temperature, a few small pieces of film 2 still adhered to the substrate. This allowed for a profilometry measurement of film thickness and surface roughness on these adhered flakes. The average thickness and rms roughness measured using this technique were  $3.8 \pm 0.5 \mu\text{m}$  and  $144 \pm 26 \text{ nm}$ , respectively. These directly measured values are in good agreement with those obtained from the model ( $3.8 \mu\text{m}$  and  $130 \text{ nm}$ , respectively).

In conclusion, optical pyrometry has been used as an effective *in situ* technique for monitoring thickness and surface roughness of diamond films on Ti-6Al-4V alloy substrates. The model used to extract these properties has been developed for the case of an absorbing substrate and for a pyrometer positioned at arbitrary angles with respect to the substrate normal. The technique has proven to be potentially useful for understanding the nucleation and growth kinetics of CVD-grown diamond films.

This research was supported by the Alabama NASA-EPSCoR program under Grant No. NCC5-165. One of the authors (S.C.) acknowledges support from the Alabama Space Grant Consortium, NASA Training Grant No. NGT5-40018. One of the authors (W.C.) acknowledges support from the NSF-REU Site award under Grant No. DMR9619405.

<sup>1</sup>A. J. SpringThorpe, T. P. Humphreys, A. Majeed, and W. T. Moore, Appl. Phys. Lett. **55**, 2138 (1989).

<sup>2</sup>K. A. Snail and C. M. Marks, Appl. Phys. Lett. **60**, 3135 (1992).

<sup>3</sup>Z. L. Akkerman, Y. Song, Z. Yin, F. W. Smith, and R. Gat, Appl. Phys. Lett. **72**, 903 (1998).

<sup>4</sup>S. A. Catledge and Y. K. Vohra, in *Thin Films-Stresses and Mechanical Properties VII*, edited by R. C. Cammarata, E. P. Busso, M. Nastasi, and W. C. Oliver (Materials Research Society, Pittsburgh, 1998), Vol. 505.

<sup>5</sup>Z. Yin, Z. L. Akkerman, F. W. Smith, and R. Gat, Mater. Res. Soc. Symp. Proc. **441**, 653 (1997).

<sup>6</sup>Z. Yin, H. S. Tan, and F. W. Smith, Diamond Relat. Mater. **5**, 1490 (1996).