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Citation: *Journal of Applied Physics* **77**, 5119 (1995); doi: 10.1063/1.359322

View online: <http://dx.doi.org/10.1063/1.359322>

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Bias induced diamond nucleation studies on refractory metal substrates

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(Received 24 October 1994; accepted for publication 6 January 1995)

The carbide forming nature of the substrate appears to be an important property when performing bias-enhanced nucleation (BEN); therefore, various refractory metals were studied since they are known carbide formers. Nucleation densities approaching $1 \times 10^{10}/\text{cm}^2$ were observed on both hafnium and titanium. The nucleation density on tantalum, niobium, and tungsten was enhanced to a lesser extent in descending order of influence, respectively. An induction time prior to the onset of significant diamond nucleation was observed on the refractory metals as well as on silicon and may be reliant upon the formation of a critical carbide thickness. Shorter induction times were observed for silicon which may be explained since this material forms a carbide of typically only several nanometers in thickness as opposed to the refractory metals which may form carbides on the order of several microns in thickness. Also, a strong correlation was observed between the carbide heat of formation and the nucleation densities at 60 min of BEN. These findings verify the relevance of a carbide formation to diamond nucleation via BEN and also provides a clue as to the mechanism(s) by which diamond is nucleating. © 1995 American Institute of Physics.

I. INTRODUCTION

To form diamond via chemical vapor deposition, a carbon containing gas such as methane must be utilized and substrate temperatures generally must be greater than 600 °C. In this carbon containing high temperature process environment it is expected that carbide phases will form on the substrate when they are thermodynamically stable. These carbide phases have been observed via x-ray diffraction (XRD)¹ and surface sensitive analytical techniques such as x-ray photoelectron spectroscopy (XPS)^{2,3} and Auger electron spectroscopy (AES).³

An understanding of how the formation of a carbide influences diamond nucleation is important if improvements in nucleation are to be achieved. Silicon substrates have been used extensively for diamond deposition based on this material's predominance in the microelectronics industry. High-quality single crystal silicon wafers are also economically available which make them attractive for diamond growth development. Results from the initial diamond research on silicon indicate that a silicon carbide interlayer formed between the diamond film and the silicon substrate. These interfacial layers have been detected via transmission electron microscopy and various surface sensitive analytical techniques. In the case of silicon, they have been typically less than a few hundred angstroms in thickness.⁴ This thin interlayer was difficult to observe using XRD, the standard analytical tool used for phase identification.

Surface analytical studies on diamond scratched silicon substrates have been undertaken to confirm the formation of this carbide and to determine its relevance to diamond nucleation.^{2,3} This work^{2,3} revealed the formation of a car-

bide prior to detecting the presence of diamond suggesting that diamond may have been nucleating on the carbide. It should be noted though that very early during nucleation the presence of diamond is difficult to observe since the quantity of diamond present may be below the sensitivity of the typical analytical instrumentation used for these studies. This stipulation makes it difficult to altogether rule out the possibility that diamond may be nucleating on the silicon directly rather than the carbide phase(s). This also holds true for other carbide forming substrates such as the refractory metals. However, during diamond deposition on refractory metals substrates Joffreau *et al.*¹ observed a correlation between diamond nucleation and the kinetic properties of the resulting carbides. This alludes to the possibility that the resultant carbide is a principle component which influences diamond nucleation. In this study the thickness of the carbide layer formed via the chemical vapor deposition (CVD) environment is on the order of several microns and was confirmed using XRD. Although silicon and the refractory metals are similar in that they both form carbides, these materials are different in that they possess unique carbide structures and material properties. Much may be gained from a better understanding of diamond nucleation if one studies and compares the attributes of diamond nucleation on various refractory metals using bias-enhanced nucleation (BEN) such as that performed by Joffreau *et al.*¹ using hot filament CVD.

Refractory metal carbides are characterized by their high melting points which relate directly to their high hardness, thus making them excellent candidates for wear and erosion resistant applications. They also possess good thermal and electrical conductivity.⁵ Refractory metal carbides have been refined and synthesized for nearly a century and have been studied intensively for decades in order to take advantage of these unique properties. Various methods of producing transition metal carbides have been demonstrated. These are (i)

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synthesis from the elements, (ii) reduction of oxides, (iii) deposition from the gas phase, (iv) electrolysis of molten salts, and (v) chemical precipitation.^{6,7} The most popular technique has been the reduction of oxides which involves a metal-oxide reduction process utilizing a carbon containing gas. Due to its relevance of the subject matter of this research, the more recent literature concerning refractory metal carbide formation via deposition from the gas phase will be discussed briefly.

Chemical vapor deposition has been used to form refractory metal carbide hard coatings for wear-related applications.⁸⁻¹⁰ In this process, gas sources are used that contain the metal and carbon for the subsequent carbide deposition. These are typically halogenated gases but methane and hydrogen are also commonly used. The deposition environment includes pressure of typically 1–100 Torr and substrate temperatures from 750 °C to as high as 1600 °C. For hard coating applications on materials not suited for high temperatures, a recent study has revealed that refractory metal carbides may be formed with substrate temperatures of less than 500 °C.¹¹ Dimethyl ether is used as the carbon source for this process.

The interaction of the carbon with the metallic lattice of the refractory carbides has been studied to gain insight into the type of bonding that exists in these compounds.⁶ It has been argued as to whether the carbon atoms are acting as electron acceptors or themselves transferring electrons during bonding. The importance of understanding the bonding nature of these compounds may help to explain this class of material's unique properties. Much of this work has concluded that the metallic lattices are stabilized by electron transfer from the carbon atoms. The refractory metal carbides are termed as interstitial compounds since the carbon atoms locate at the interstitial sites of the metallic lattice. This is contrary to silicon carbide in which the silicon and carbon atoms situate themselves on alternate sites in the diamond structure. Many times these interstitial sites are vacated which leads to stoichiometric imbalances. This has led to refractory metal carbides also being regarded as defect compounds. Also, with regard to the refractory metals that possess a higher occupancy of electrons in the *d*-orbital, more complex crystal structures may result.

Typically the refractory metal carbides exist in either the sodium chloride (B1) or the nickel arsenide (B8) crystal structures. The monocarbides (MeC) are B1 type with the carbon atoms occupying the octahedral positions in the metal lattice. Tungsten carbide does not fit this general rule but instead forms in the simple hexagonal structure. This alludes to an important aspect of the refractory metal carbides. When considering the refractory materials situated in groups IVB, VB, and VIB an increased number of stable carbide phases results in this ascending order, respectively. The group IVB materials (i.e., Ti, Zr, and Hf) exhibit only the monocarbide phase. While, groups VB (i.e., Ta, Nb, and V) and VIB (i.e., Mo, W, Cr) also form the subcarbides (Me₂C), which typically form in the B8 crystal structure. In addition to the complex carbide phases arising with a higher *d*-orbital electron concentration, the width of the monocarbide phase field decreases steadily from groups IVB to group VIB.

The subcarbides formed during high temperature processing of groups VB and VIB, are characterized by the carbon atoms randomly situated on half the octahedral sites. It has been shown, however, that at lower temperatures the carbon atoms may become ordered.¹² In this case the Mo₂C and Nb₂C transform to the orthorhombic crystal structure while the Ta₂C and the W₂C transforms to the trigonal crystal structure. In addition to the monocarbide and subcarbide phases possible in the group VIB refractory metals, more complex carbide phase stoichiometries may form. The possibility of forming these various carbide phases makes it difficult to isolate the particular phase on which diamond may be nucleating. Temperature and gas ratio variations across the substrate may result in multiple carbide phases which further hinders diamond nucleation studies on the refractory metals. In the absence of forming a monophase carbide surface of known stoichiometric composition only a general interpretation of the diamond nucleation events may be obtained on these substrates.

The present study was undertaken to investigate the influence of the refractory metals on bias-enhanced nucleation (BEN). BEN has been observed to enhance the diamond nucleation density on unscratched Si(100) substrates^{13,14} and it was later discovered that epitaxial diamond may form on these substrates via a carburization step followed by this nucleation pretreatment.¹⁵ This process involves applying a negative bias to the substrate holder while it is immersed in a CH₄/H₂ plasma in order to promote diamond nucleation. In a study of BEN on copper substrates by these authors, the negative substrate bias was found to be relatively ineffective in promoting diamond nucleation.¹⁶ Thus, the carbide forming nature of the substrate has been speculated to strongly influence the nucleation efficiency during the biasing process. The variation in the carbide forming nature of the refractory metals should thus reveal a correlation with the nucleation phenomena via BEN. This should make it possible to gain further insight into this pretreatment process and diamond nucleation in general as well as to investigate potential heteroepitaxial substrates using this pretreatment technique.

II. EXPERIMENT

Bias-enhanced nucleation (BEN) and diamond deposition was performed in a microwave plasma CVD chamber purchased from Applied Science and Technology, Inc. The growth system has been discussed in greater detail previously.¹³ In general, a plasma is generated by a 2.45 GHz microwave source in a gas mixture of methane and hydrogen. Also, the growth chamber is joined to an analytical chamber by way of a transfer tube, thus making it possible to perform *in vacuo* surface analysis. The substrate is affixed to a molybdenum substrate holder which rests horizontally on a separately pumped tantalum can that contains a heating filament. BEN was performed as a pretreatment routine to promote diamond nucleation. A negative dc bias was applied to the tantalum can and substrate holder, while the positive potential was connected to ground. An explanation as to the proposed mechanisms responsible for diamond nucleation

TABLE I. Conditions under which bias-enhanced nucleation and diamond deposition were performed on the refractory metal substrates.

Process parameters	Bias conditions	Deposition conditions
Microwave power	900 W	900 W
CH ₄ /H ₂	5%	1%
Pressure	15 Torr	25 Torr
Substrate temperature	~725 °C	~700 °C
Bias voltage	~250 V _{DC}	Floating
Bias current	~100 mA	N/A
Sample position	Immersed	Immersed

via BEN has been discussed previously.^{17,13,16} Table I indicates the BEN and diamond deposition conditions utilized in this study.

The refractory metals used in this study were hafnium, titanium, tantalum, niobium, and tungsten and were studied within a short time span so the effects from growth system variations or the other external influences would be minimized. These substrates were chosen to examine each of the groups of refractory metals (i.e., groups IVB, VB, and VIB) but were chosen arbitrarily within each group. Hafnium was an exception of this since it was used in the later phase of this experimental sequence to confirm the possible correlations to be discussed later.

The substrates were polished using SiC followed by diamond media and further polished using 0.05 μm alumina powder suspended in de-ionized water. The alumina was used in the final polishing procedure to ensure that very little residual diamond would be present on the substrates. Diamond residue has been speculated to act as diamond nucleation seeds;¹⁸ therefore, finishing the polishing procedure with alumina aided in eliminating this possibility. It should be added that alumina has also been observed to enhance the diamond nucleation density, however, to a much lesser extent.¹⁸ As will be shown shortly, the nucleation densities were much higher than expected if residual diamond or alumina were responsible for diamond nucleation. The substrates were then solvent cleaned using trichloroethylene, acetone, methanol, and 2-propanol, consecutively. A de-ionized water rinse was performed on the substrates just prior to entering into the growth chamber.

A. Nucleation density vs bias time

Each of the refractory metal substrates was subjected to varying BEN times followed by 30 min of diamond deposition to obtain data of the nucleation density versus bias time. The short deposition period prevented the particles from coalescing and enabled an accurate account of the density of diamond nuclei that were observed by scanning electron microscopy (SEM). The initial diamond was found to have formed on the edges of these substrates and nucleation proceeded toward the center. The nucleation density measurements were undertaken at the center portion of the substrates and multiple sampling areas were examined to ensure consistent results. The nucleation density versus bias time plot provides insight into the effectiveness of BEN among the refractory metal substrates. This data will be compared to

IIIB	IVB	VB	VIB	VII	VIII	IB	IIIB
Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
La	Hf	Ta	W	Re	Os	Ir	Pt
							Au
							Hg

FIG. 1. Nucleation density vs bias time for various refractory metals compared to silicon and copper.

similar data obtained on silicon and copper. X-ray diffraction (XRD) was then used to determine the phases present following BEN and diamond deposition.

B. *In vacuo* surface analytical series vs bias time on titanium

BEN of titanium was studied more extensively due to the exceptional influence it had on the BEN process which was uncovered in the initial experimentation. A titanium substrate was polished and cleaned similar to the earlier work on the refractory metals and subsequently entered into the growth chamber. The substrate was transferred under vacuum at various time intervals during BEN to an analytical chamber and analyzed utilizing both x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). At the completion of analysis the substrate was transferred back to the growth chamber and BEN was continued until the next time interval had expired. The intermittent time steps were 0, 5, 15, 30, 60, 120, 180, and 300 min, consecutively. XPS binding energies were used to identify the surface constituents and phase formations, while the AES fine structure was used to reveal the form of the carbon of this region as well as the presence of any carbon-based phases.

III. RESULTS

A. Bias-enhanced nucleation of diamond on refractory metals

The refractory metals that were targeted in this study are shown in Fig. 1 as they are situated in the periodic table. The plot of nucleation density versus bias time for these refractory metals compared to silicon and copper is shown in Fig. 2. The diamond nucleation density on copper substrates as discussed previously is relatively unaffected by the application of a negative substrate bias per these experimental conditions.¹⁶ In contrast, silicon has proven to be an ideal substrate for BEN.^{13,14} The individual plots of these materials were curve fitted with correlation coefficients greater than 0.85 and is meant to give a general interpretation of the relative influence of the negative substrate bias for establishing diamond nuclei. The nucleation densities at 60 min of substrate biasing were used to formulate a sequential ordering of the refractory metals according to their effect on diamond nucleation via BEN. The nucleation density at this bias time was chosen since any further substrate biasing did not appreciably increase the nucleation density. The initial experiments revealed that titanium substrates resulted in a diamond nucleation density approaching $1 \times 10^{10}/\text{cm}^2$ at this

FIG. 2. Surface analytical techniques were used to identify the elements and the form of the carbon present on the titanium substrates as seen in the (a) XPS and (b) AES spectra, respectively. This graphic reveals the formation of titanium carbide in as early as 5 min of BEN. Also, an induction time before the onset of significant diamond nucleation is evident between 30 and 60 min of biasing. At this time the C-C peak notably increases which is commensurate with a dramatic increase in the nucleation density.

bias time. The niobium, tantalum, and tungsten yielded decreasing nucleation densities, respectively. This initial survey study of these elements revealed a possible correlation to a refractory metal material property to be discussed later. This led to the addition of hafnium to this study in order to confirm these possible correlations. The hafnium was predicted to surpass the titanium nucleation densities at prolonged BEN times and this was confirmed via experimentation.

B. *In vacuo* surface analytical study of titanium

The results of this aforementioned study led the authors to perform a more detailed study of diamond nucleation on titanium during BEN. The objective of this research was to gain a broader comprehension of the diamond nucleation events during the negative substrate bias pretreatment. Both *in vacuo* XPS and AES were used to characterize this substrate during BEN at various bias time intervals as shown, respectively, in Figs. 3(a) and 3(b). The escape depth of the photoelectrons and Auger electrons have been estimated to be 30 Å from the surface thus allowing a surface sensitive study of BEN on titanium.¹⁹ The 0 min XPS spectra revealed the presence of chemisorbed oxygen and a nondiamond advantageous surface carbon on the titanium substrate. After 5 min of BEN, TiC was observed to have formed. The peak positions identified throughout this time series study were referenced to those reported in Ref. 20. Oxygen was also detected and is believed to have been adsorbed during transfer from the growth chamber to the analytical chamber. If oxygen were present in the growth chamber during BEN and the short diamond deposition procedure, it is assumed that chemisorbed oxygen would be observed; however, only physisorbed oxygen was detected via XPS. There was only a slight change in the XPS spectra up to 30 min of BEN. Likewise, the AES spectra also indicated TiC with only a

FIG. 3. The transition metal portion of the periodic table indicating the refractory metals investigated in this research.

subtle change in the spectral features throughout this bias duration. Between 30 and 60 min of biasing an increased presence of carbon was observed which eventually led to a strong diamond peak at 3 h of BEN. The AES fine structure at 3 h of BEN was indicative of diamond.

IV. DISCUSSION

A. Bias-enhanced nucleation on refractory metals

The periodic trends of the refractory metal and refractory carbide material properties are generally known to those who have studied these materials. With respect to diamond nucleation on these materials it may not be unreasonable to expect the nucleation processes to be influenced by a similar periodicity. Typical pretreatment techniques to enhance diamond nucleation utilize diamond media as a precursor to diamond formation. This directly influences diamond nucleation in that nucleation densities pretreated with diamond media are approximately three orders of magnitude higher than nonpretreated substrates. BEN does not require a deleterious pre-

treatment or external carbon precursor that may influence diamond nucleation; nucleation may be enhanced on pristine substrates via this process.

The authors have speculated that an important attribute for enhanced diamond nucleation via the negative substrate bias is the ability to form a stable carbide.¹⁶ Thus, the refractory metals as shown in Fig. 1 were chosen for this study because of their carbide forming nature. It is fortuitous to have at our disposal this class of material with well-defined periodic attributes that allow the authors to use BEN to study diamond nucleation. This may reveal the mechanism(s) by which diamond nucleation is occurring via the negative substrate bias and may lead to a better understanding of diamond nucleation in general. This study also offers insight into the most appropriate substrates for further heteroepitaxial diamond nucleation studies.

B. Refractory metal material properties and diamond nucleation

It was revealed that diamond nucleation on Hf and Ti was significantly enhanced followed by Ta, Nb, and W, in order of influence, respectively. This substantiates the claim that the carbide forming nature of the substrate is important for BEN. The formation of a carbide on the refractory metal substrates was confirmed by XRD. Also, the *in vacuo* study of titanium proved that a carbide was formed during BEN on this material in as early as 5 min of biasing. Thus, it is presumed that the carbides observed via XRD for all the substrates were formed primarily during the negative substrate bias pretreatment. This carbide layer may possibly be several microns in thickness. This is based on past work¹ and since XRD per this study was able to detect the presence of carbide phases on the refractory metal substrates. On the otherhand, the carbide forming silicon substrates have been observed to form a carbide of only several nanometers in thickness.⁴

The nucleation density versus bias time graphic (Fig. 2) indicates that longer bias durations are necessary before a significant increase in the nucleation density is observed on the refractory metal substrates when compared to silicon. This was also observed in Fig. 3 in which a dramatic increase in the C-C peak was observed between 30 and 60 min of biasing on titanium. This increase in the C-C peak corresponded to a dramatic increase in diamond nucleation. This induction time prior to the onset of significant diamond nucleation may be reliant upon the carbide formation. It is suggested that a critical carbide thickness must be formed before significant diamond nucleation may occur. The lower induction times observed for silicon when compared to the refractory metals in general may be explained by the much thinner carbide layer that forms on silicon. It is proposed that the surface carbon via the methane in the CVD environment is transported into the substrate very early during BEN forming the particular carbide. The carbon diffusion rate through the carbide as opposed to the noncarburized substrate is several orders of magnitude lower. Thus, the formation of a carbide in this case may enhance the lifetime of the surface carbon since the carbon transport into the carburized sub-

FIG. 4. Plot of the nucleation density at 60 min of BEN vs the carbide heat of formation. This graphic reveals a relationship between BEN and this material property.

strate is dramatically lessened. This free surface carbon may then be utilized for the formation of stable diamond nuclei.

The relatively thick carbide that forms on the refractory metal substrates may now explain the longer induction times prior to the onset of significant diamond nucleation compared to silicon. However, there was also a varying influence on the diamond nucleation density for the refractory metals. The influence of this biasing pretreatment on diamond nucleation was found to correspond to the position of these substrate materials in the periodic table. The group IVB, VB, and VIB metals follow a trend of most influenced to least influenced, respectively. In regard to this observation, material properties were sought that would show a correlation to the degree of influence of BEN. The carbide heat of formation, ΔH_f^{298} , per metal atom was found to correlate to the nucleation density values at 60 min of biasing as is shown graphically in Fig. 4. Each of the carbide phases observed via XRD was plotted in this graphic since it was difficult to determine their relative amounts or the most abundant surface region phase(s). The refractory metals forming a more stable carbide (i.e., more negative ΔH_f^{298}) resulted in the highest diamond nucleation densities. This correlation led the authors to investigate hafnium which exhibits a more stable carbide than titanium. As predicted the hafnium yielded nucleation densities greater than that of titanium (Fig. 2).

Although a correlation was found to exist between the carbide heat of formation and the nucleation density at prolonged bias durations for the refractory metals, silicon did not fit this data. Silicon possesses a comparable carbide heat of formation to that of tungsten yet was much more effective as a substrate. This indicates another attribute possessed by silicon that is influencing diamond nucleation via BEN. One possible attribute that should be considered is the crystal structure of silicon carbide which is the tetrahedrally coordinated zinc blend structure. This structure is similar to diamond but contains both silicon and carbon rather than entirely carbon. The refractory carbides, however, exist predominantly in either the rock salt (B1) or nickel arsenide (B8) structure.

The correlation uncovered between the carbide heat of formation and the nucleation density for the refractory metals again indicates the importance of the carbide formation of

the substrates on the bias-enhanced nucleation of diamond. Substrates capable of forming carbides in general have a high affinity for carbon, and the substrates possessing the more negative carbide heat of formation values have the greatest affinity. It was proposed that the induction time prior to the onset of significant diamond nucleation was reliant upon forming a critical carbide thickness. Once this carbide layer is formed, the free surface carbon may then be utilized to form stable diamond nuclei. We further speculate that once this induction time is surpassed the substrates with a greater affinity for this free surface carbon (i.e., more negative ΔH_f^{298}) enhances the diamond nucleation process resulting in higher nucleation densities.

V. SUMMARY

This research has confirmed that the carbide forming nature of the substrate is an important attribute of the substrate when using bias-enhanced nucleation. Nucleation densities approaching $1 \times 10^{10}/\text{cm}^2$ were observed on both hafnium and titanium. The nucleation density on tantalum, niobium, and tungsten was also enhanced in descending order of influence, respectively. An induction time prior to the onset of significant diamond nucleation was evidenced in the nucleation density versus bias time graphic (Fig. 2) and is speculated to be dependent upon the formation of a critical carbide thickness. Silicon exhibits a carbide of typically several nanometers in thickness as opposed to the refractory metals which may form carbide layers on the order of several microns in thickness. This may explain the shorter induction times on silicon compared to the refractory metals. Also, the carbide heat of formation of the refractory metals was determined to correlate to the nucleation density values taken at 60 min of BEN. This again verifies the relevance of a carbide formation to diamond nucleation via BEN and also provides a clue as to the mechanism(s) by which diamond is nucleating.

ACKNOWLEDGMENTS

The authors would like to thank M. Veil for her assistance during experimentation. We also gratefully acknowl-

edge the financial support of this research which was provided in part by BMDO-IST through ONR and the Kobe Steel, Ltd. Professorship at NCSU.

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