SF 298 MASTER COPY KEEP THIS COPY FOR REPRODUCTION PURPOSES

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
8 Aug 97

3. REPORT TYPE AND DATES COVERED
Final Technical 1 Aug 95 - 31 Jan 97

4. TITLE AND SUBTITLE
DURIP95 NANO-MODULATED CERAMIC PROTECTIVE FILMS ON GLASS SUBSTRATES

5. FUNDING NUMBERS
F49620-95-1-0480

6. AUTHOR(S)
Professor Henry W. White

AFOSR-TR-97
0336

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)
The Curators of the University of Missouri
for the University of Missouri-Columbia
310 Jesse Hall
Columbia, MO 65211

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NA
110 Duncan Avenue, Suite B115
Bolling AFB DC 20332-0001

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
F49620-95-1-0480

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Air Force position, policy or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

19971002 143

13. ABSTRACT *(Maximum 200 words)*

The primary objectives of this research effort were to synthesize and characterize several kinds of ceramic films, and to develop in situ techniques for monitoring the growth process of these coatings. Chemical vapor deposition was used for film growth. An FT-IR spectrometer was configured for in situ monitoring of chemical reactions and film composition during growth. The work contributes to the Air Force structural materials program, particularly to the area of improved protective coatings for glass and related materials. Capabilities reported include the ability to monitor chemical composition during thin film growth. Chemical species on the surface of a growing diamond film on a sapphire substrate were monitored in situ using grazing incidence infrared reflectance spectroscopy. Continuation of this work will evaluate the use of polarization modulation reflectance for in situ monitoring. This work will assist in the development of new materials for coatings and the establishment of new research capabilities in the fabrication of nano-modulated ceramic/oxide coatings on a variety of materials of interest to the Air Force.

14. SUBJECT TERMS
coatings, films, fabrication, ceramic, glass, monitor, chemical composition, growth process, infrared, reflectance, in situ

15. NUMBER IF PAGES
6

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT
UNCLASSIFIED

20. LIMITATION OF ABSTRACT
UL

NSN 7540-01-280-5500

DTIC QUALITY INSPECTED 4

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

FINAL TECHNICAL REPORT

Agency Name	US Department of Air Force
Grant No.	AFOSR F49620-95-1-0480
Project Title	DURIP95 NANO-MODULATED CERAMIC PROTECTIVE FILMS ON GLASS SUBSTRATES
Award Dates	1 Aug 95 - 31 Jan 97 (as extended)
Program Manager	Alexander Pechenik, NA (202) 767-4987
Grantee	The Curators of the University of Missouri, for UM-Columbia
Principal Investigator	Professor Henry W. White Department of Physics, University of Missouri, Columbia, MO 65211 Tel (573) 882-7241 FAX (573) 882-7241 e-mail physhw@showme.missouri.edu
MU Digit Acct. Nos.	C-5-32320-7700; C-2-00074-7772 (match)

Acquired Equipment

Name	Manufacturer	Cost
Fourier Transform Infrared (FT-IR) Spectrometer Systems, comprised of the following major items, purchased as a package from ATI Mattson:		
Infinity Model FT-IR Spectrometer System	ATI-Mattson	
Galaxy Model FT-IR Spectrometer System	ATI Mattson	
Quantum Infrared Microscope	ATI-Mattson	
Real-time sampling electronics	ATI-Mattson	
Purge gas generator for FT-IR spectrometers	Balston Inc.	
	Subtotal	$103,100.00
(UMC PO # C665278)		
Computer, Model P5-100	Gateway 2000	2,095.00
(UMC PO # C764165)		
Pressure Meter	MKS Instruments	3,053.05
(UMC PO # C769289)		
Sample Transporter	Thermionics Northwest	2,071.73
(UMC PO # C769493)		
Sample Chamber	Nor-Cal Products	6,880.22
(UMC PO # C770243, partial cost only)		
Total Equipment Amount		$117,200
Less University of Missouri Cost Sharing		$ 50,000
AFOSR Award Amount		$ 67,200

Overall Objectives

The primary objectives of this research effort were to synthesize and characterize several kinds of ceramic films, and to develop in situ techniques for monitoring the growth process of these coatings. Chemical vapor deposition was used for film growth. An FT-IR spectrometer was configured for in situ monitoring of chemical reactions and film composition during growth. The work contributes to the Air Force structural materials program, particularly to the area of improved protective coatings for glass and related materials. Capabilities reported include the ability to monitor chemical composition during thin film growth. Chemical species on the surface of a growing diamond film on a sapphire substrate were monitored in situ using grazing incidence infrared reflectance spectroscopy. Continuation of this work will evaluate the use of polarization modulation reflectance for in situ monitoring. This work will assist in the development of new materials for coatings and the establishment of new research capabilities in the fabrication of nano-modulated ceramic/oxide coatings on a variety of materials of interest to the Air Force.

Special Circumstances Regarding Equipment Acquisition

ATI Mattson offered, and the University of Missouri accepted, an option that provided two FT-IR spectrometers instead of one, at an overall increase in cost of less than $5,000 (i.e. 5% of total cost). This option allowed University of Missouri to have a new-to-the market, high performance model FT-IR dedicated to in situ measurements located on the chemical vapor deposition growth chamber, and a second (demonstrator model) FT-IR dedicated the infrared microscope located separately. This option had two benefits: (i) the physical arrangement greatly reduced the amount of time that would be required for continued re-alignment if only one FT-IR was available, and (ii) the new model FT-IR had specifications superior to the one specified in the proposal.

Late in the grant period, Hinds International reversed its recommendation for the feasibility of gold coating the backside of a ZnSe crystal that would be the polarizer element in the new photoelastic modulator. The revised recommendation was based on their risk assessment for providing a unit that would meet reasonable specifications for minimum optical transmission, associated with possible degradation of the ZnSe crystal surface-gold film boundary. Since an assessment of the benefits associated with using a double pass through the modulator (to attain polarization modulation at wavenumbers below 1200 cm-1) could be made in our laboratory for the proposed effort by use of an external mirror and an existing polarization modulation unit, it was deemed that a new polarization modulation unit should not be ordered.

List of Changes to the Equipment List

Two FT-IR spectrometers were obtained rather than one, and the photoelastic modulator with an element gold coated on the backside was not purchased, as discussed above. A computer printer, and an optical table suitable for the infrared microscope system with the microscope attachment, were obtained from other sources. The net amount of funds saved by these changes were used to upgrade to a sample chamber with better optical access (NorCal), with a sample transporter (Thermonics Northwestern) and pressure metering (MKS) for in situ studies.

Research Projects for which the Equipment was Used

The equipment was used on several research projects involving both in situ monitoring of film growth on substrates using chemical vapor deposition (CVD) using the new FT-IR spectrometer, and for ex situ infrared studies of films fabricated by CVD and pulsed laser deposition (PLD) in our laboratory using the FT-IR with infrared microscope. Other techniques in other laboratories at the University of Missouri were also used. In each project the spectral data were obtained by grazing incidence reflectance without the use of polarization modulation, in large measure because interesting information was being obtained at a good rate, and because these studies provided a baseline of information that will aid considerably in the interpretation of spectral data obtained by the polarization modulation technique. In other words, (i) the possibility for in situ monitoring of CVD film growth using infrared spectroscopy has been demonstrated, but the range of techniques (i.e., polarization modulation) that will be investigated has not yet been completed at the time of this report. (ii) The infrared microscope was of considerable benefit to the proposed effort in the evaluation of thin film growth on several types of substrates. A evaluation of the polarization modulation technique and its comparison with the grazing reflectance technique will follow the reflectance studies now being completed.

Brief summaries of the two major reflectance projects are provided below.

(1) Diamond growth on sapphire substrates

In situ FT-IR spectroscopy using the Infinity Model ATI Mattson spectrometer with a high grazing angle of incidence was first evaluated in a project to monitor the growth of diamond films on sapphire substrates. A schematic of the essential parts of the experimental setup is shown in Fig. 1. The advantage of this technique over the use of polarization modulation is the higher optical throughput and ease of obtaining extended range below 1200 cm-1, and for this reason was begun first. The main interest in all of these applications was determination of the chemical nature of the adsorbates on the growing film surface and the composition of the film itself, rather than species in the gaseous plasma. Molecular species in the gaseous plasma can be determined by other means, such as emission spectroscopy that is available in the laboratory.

An electron cyclotron resonance, plasma assisted CVD system located in the laboratory was used for gas molecule dissociation in order to deposit carbon species from methane. The most abundant carbon-containing gaseous species present in most activated CVD systems are methyl radicals and acetylene molecules that are also considered to be predominant growth precursors for diamond growth. Spectroscopic data were obtained for a range of substrate temperatures, nominally in the range of 500°C. The methane/hydrogen gas mixture was 1% methane at a total pressure of 500 mTorr.

The grazing incidence angle was 80 degrees, which is a reasonable value for substrates that are not metallic. A subtraction method was employed to eliminate background effects as well as to ascertain absorption by the bulk substrate. Time for a typical growth run would be about ten hours, with spectra taken every hour. Spectra could have been taken more often, even on a continuous basis; however, once per hour was sufficient and minimized undesirable deposition of coating of the infrared transmitting windows.

Deposition of diamond, diamond-like films and graphitic-like films was determined by ex situ Raman, scanning electron microscopy and atomic force microscopy. Figure 2 shows a Raman spectrum of a small crystallite of diamond on a sapphire substrate. The peak located near 1333 cm-1 is broad (20 cm-1) due the small size of the crystallite, and the background is high due to the high fluorescence for the sapphire substrate.

Figure 3 shows an in situ infrared spectrum taken after six hours of growth. A broad, low intensity absorption band located near 1020 cm-1 is apparent with a width of about 80 cm-1. This absorption band is assigned as a CH3 rocking mode that usually appears in the 1010 to 1070 cm-1 region. This assignment is supported by the appearance of another absorption band around 1400 cm-1 with a width of 10 cm-1 that is associated with an H-H bending vibration in the same functional group. There are also two broad, low intensity broad bands in the 2800 - 2970 cm-1 and 3000 - 3300 cm-1 regions that are due to C-H stretching vibrations in sp3 and sp bonded hydrocarbon, respectively. These two bands were present throughout the deposition and their intensities increased with time. Figure 4 shows another spectrum of the same sample under the same deposition conditions (power, gas flow, etc.) taken a few hours after the one shown in Fig. 3. An enhancement in the intensities of several peaks (e.g., 1400 and 2900 cm-1) can be seen. This behavior is interpreted as the formation of a thin film with bonding features similar to those of species present on the surface of the growing film.

The spectra showed that identification of adsorbates on the surface that were involved in film growth could be detected during active plasma deposition with grazing incidence spectroscopy, and that the species present changed systematically during the growth period. The spectra could be understood and interpreted on the basis that no major absorptions were occurring from species in the plasma. Evidently, the enhancement factor (ten or so, estimated) gained from grazing incidence geometry on a metallic-like substrate surface was sufficient to give absorption signals from the surface, and the absorption from the plasma is sufficiently weak due to the traversing path of the beam in the plasma that no competing absorptions from plasma species interfered in the spectral regions of interest.

Results from real time monitoring of the adsorbed species on the substrate showed that the dominant growth precursor to diamond is the methyl radicals present in the plasma. The results showed that there was an initiation, or induction, time of several hours that elapsed prior to deposition of diamond on the substrate. The precursor film was graphitic in nature. It is reasonable to assume that formation of the precursor film is accompanied by carbon diffusion into the substrate, with the buildup of a graphitic-like layer that can support diamond growth on a substrate such as sapphire. This model would explain the poor adhesion to the substrate displayed by CVD grown diamond.

Preliminary results have been submitted for presentation at the Material Research Society meeting, December 1-5, 1997, in Boston, Mass. Final results will be published elsewhere.

(2) Diamond growth on steel and other metal substrates

In situ studies similar to those on sapphire have been made with other substrates, with considerable preliminary data for steel, and with some preliminary results for nickel and copper substrates. Again, an initiation phase is observed. These grazing incidence reflectance studies are nearing completion, prior to an evaluation and comparison of the polarization modulation technique for monitoring the growing film. Preliminary calculations have been made for infrared frequencies associated with possible modes for sp3 bonded groups on the surface of a diamond film to compare with the experimental results. Results of this work will be submitted for publication.

Acknowledgements

Optical equipment for these projects was provided by the DURIP award AFOSR F49620-95-1-0480. Costs for expendables, personnel, and other equipment were provided in part by grant DAAH04-94-G-0305 from the U.S. Army Research Office, Research Triangle Park, N.C.

Fig.1

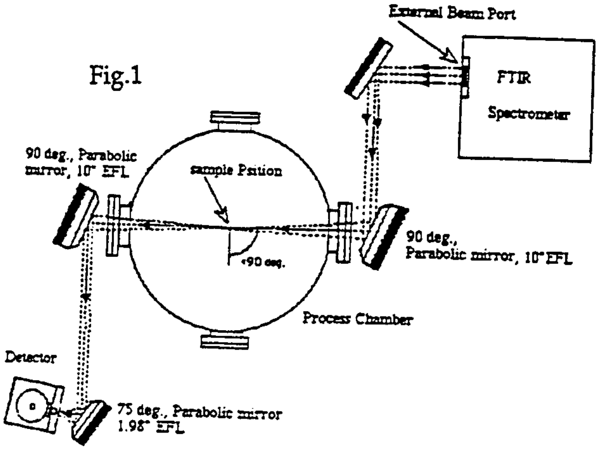

Fig.2

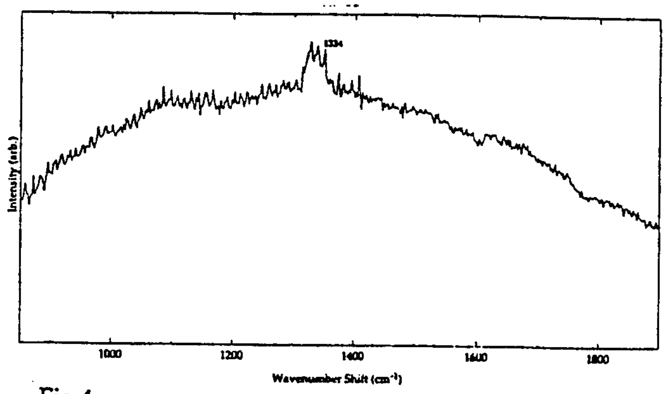

Fig.3

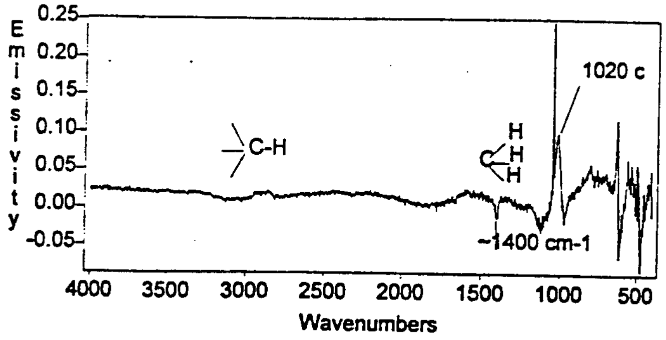

Fig.4

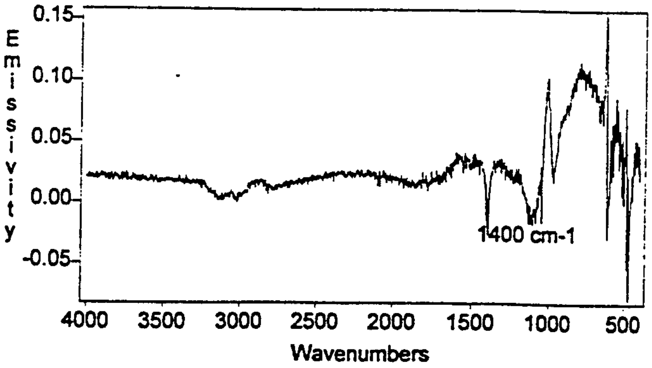

Fig. 1. Schematic diagram of the optical layout for monitoring diamond film growth by infrared.

Fig. 2. Raman spectrum of small diamond crystallite on sapphire. The sapphire shows considerable luminescence, and the peak at 1333 cm-1 is broadened by small crystal size.

Fig. 3. Infrared spectrum taken after six hours of growth during active CVD deposition of film.

Fig. 4. Infrared spectrum taken a few hours after that of Fig. 3, under same growth conditions.