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Evaluation of chemical and structural properties of germanium-carbon coatings deposited by plasma enhanced chemical vapor deposition

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Germanium-carbon coatings were deposited on silicon and glass substrates by plasma enhanced chemical vapor deposition (PECVD) using three different flow ratios of GeH_4 and CH_4 precursors. Elemental analysis, structural evaluation and microscopic investigation of coatings were performed using laser-induced breakdown spectroscopy (LIBS), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM), respectively. Based on the results, the coatings exhibited a homogeneous and dense structure free of pores with a very good adhesion to substrate. The structural evaluation revealed that the germanium-carbon coatings were a kind of a Ge-rich composite material containing the amorphous and crystalline germanium and amorphous carbon with the mixture of Ge–Ge, Ge–C, C–C, Ge–H and C–H bonds. The result suggested that the amorphisation of the coatings could be increased with raising CH_4:GeH_4 flow rate ratio and subsequently increasing C amount incorporated into the coating.

1. Introduction

Flying infrared (IR) systems always suffer from particle incidence when exposed to inimical environment. With increasing aerospace vehicle velocities, the environment becomes more and more severe for the IR windows materials. However, the limited available IR window materials, such as Ge, ZnS, ZnSe, due to inadequate hardness, and large refractive indexes and consequently, high reflections and low transmissions, cannot satisfy the severe requirements for the environmental applications [1]. Nowadays, the use of the coating technology is the most promising approach to improve the mechanical and optical performance of IR windows. Therefore, some varieties of protective and anti-reflective coatings that are based on the available IR highly durable materials such as diamond-like carbon (DLC) [2], boron phosphide (BP) [3], gallium phosphide (GaP) [4,5], aluminum gallium phosphide (AlGaP) [6], and germanium-carbon (Ge_{1-x}-C_x) [7–9] have been developed. Phosphorus-based coatings have relatively high refractive indexes, and don not create high transmission alone [10]. DLC has high hardness, but its poor adhesion on some IR windows materials such as ZnS, and high intrinsic compressive stress and absorption coefficient, which both prevent the growth of thicknesses greater than ~2 μm, can limit its application as a protective and anti-reflective coating [1,10,11]. In the meantime, germanium-carbon coatings have numerous attractive properties such as high durability, high hardness, low stress, light absorption, broad band IR transparency, and good adhesion on many IR substrates such as ZnS and Ge [12–14]. In particular, their refractive index can be varied in a wide range (2–4) with the ratio varying of C and Ge, thereby making germanium-carbon coatings potential candidates for the design and preparation of multilayer anti-reflective and protective coatings of IR windows [14,15]. Germanium-carbon coating could be grown in thick layers if necessary (>100 μm) [10,16]. Nowadays, there are two main methods to produce germanium-carbon coatings, including sputtering [17–21] and plasma enhanced chemical vapor deposition (PECVD) [12,22,23]. It has been reported that the refractive index of coatings deposited by PECVD can be varied over a larger range as compared to the coatings deposited by sputtering [12,16].

In general, it seems that the use of protective and anti-reflective germanium-carbon coatings can improve IR windows performance

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used under severe environmental conditions. However, in spite of the importance of this issue, few reports have been published on the general characteristics of germanium-carbon coatings deposited by PECVD method. Therefore, this study aimed at preparing germanium-carbon coatings by PECVD and their evaluation to come to a better understanding of the structure of these coatings and provide some substructure for the development of protective and anti-reflective coatings based on germanium-carbon. In this study, X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, laser-induced breakdown spectroscopy (LIBS), field emission scanning electron microscopy (FESEM), and atomic force microscopy (AFM) were employed to characterize the coatings.

2. Experimental procedures

2.1. Preparation of coatings

Germanium-carbon coatings were simultaneously deposited on both glass and Si (001) substrates by PECVD technique with a gas mixture of germane (GeH_4, 99.999%, Foshan Huate Gas, China) and methane (CH_4, 99.995%, Technical Gas Services, China) as the precursor. To this end, a parallel-plates RF glow discharge stainless steel reactor (13.56 MHz) was employed. Fig. 1 shows the schematic illustration of the apparatus configuration. The substrates were cleaned ultrasonically in acetone. Then, they were rinsed ultrasonically in the deionized water and OP-120 solution for 6 min and in the deionized water for 8 min consecutively. Finally, the substrates were dried in a clean oven under atmospheric pressure at 40 °C for 20 min. In order to perform the deposition process, after placing the samples in the reactor, the chamber was evacuated by a rotary pump to 0.13 Pa. Then, for the activation of substrate surface and consequently, the improvement of the coating adhesion, plasma etching process was done in the argon plasma environment for 3 min with condition described here: flow rate: 30 sccm; work pressure: 13 Pa; and RF power: 100 W. Then, after providing the background vacuum, at a given RF power and based on the deposition pressure and the flow ratio of gas precursors, germane and methane gases were fed into the deposition chamber under the precise control of digital mass flowmeters. The details of deposition parameters are listed in Table 1. The coatings deposited on Si substrates were chosen for structural evaluations by FTIR and Raman spectroscopies. The coatings deposited on the glass substrates were used for other measurements.

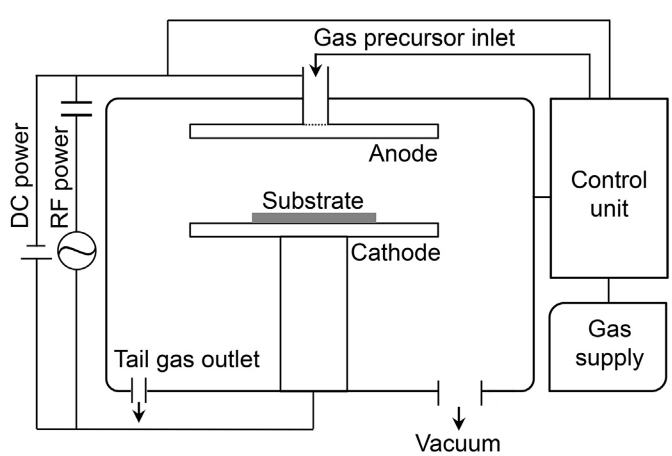

Fig. 1. Schematic illustration of PECVD apparatus configuration.

Table 1
Deposition parameters of germanium-carbon coatings.

Parameter	Sample code		
	S1	S2	S3
RF power (W)	80	80	120
Background vacuum (Pa)	0.13	0.13	0.13
Deposition pressure (Pa)	13.33	13.33	26.66
Flow rate of CH_4 (sccm[a])	0.2	0.4	2.2
Flow rate of GeH_4 (sccm)	0.5	0.4	1.1
Flow rate ratio of CH_4:GeH_4	2:5	1:1	2:1
Plate separation (mm)	20	20	20
Deposition time (min)	30	35	25

[a] Standard cubic centimeter per minute.

2.2. Characterization

2.2.1. LIBS analysis

The elemental compositions of the coatings were investigated by a LIBS apparatus (LIBSCAN100, Applied Photonics LTD, UK). A Q-switched Nd:YAG laser (Quentel, USA) operating at the wavelength of 1064 nm with pulse duration of 5–7 ns and pulse energy varies from 10 to 100 mJ was used for the ablation of the coating surface and plasma creation. To detect the elements, plasma emission was collected by an optical system and transmitted to the spectrometer.

2.2.2. FTIR evaluation

Infrared absorption spectra of the coatings were recorded using a Fourier transform infrared spectrometer (FTIR; Shimadzu, 8400S, Japan) in the 400–3500 cm^{-1} wavenumber range working at the resolution of 0.8.

2.2.3. XRD analysis

The phase structure of the coatings was studied by a grazing incidence X-ray diffractometer (GIXRD; PANalytical X'Pert Pro MPD, Netherlands) with Cu-Kα radiation (1.54060 Å) at an incidence angle of 1° in the interval $10° < 2\theta < 90°$ and the working power of 40 kV and 40 mA.

2.2.4. Raman spectroscopy

The Raman spectra were recorded in the range of 100–2000 cm^{-1} at room temperature using a Broker Senterra (Germany) Raman spectrometer equipped with high-energy laser diodes operating at a wavelength of 785 nm. The laser power density was ~1300 W/cm^2 and the spectral resolution was 3 cm^{-1}.

2.2.5. FESEM

The microscopic characteristics of the coatings were investigated by a field emission scanning electron microscope (FESEM; MIRA3-TESCAN, Czech Republic) equipped with energy dispersive spectroscopy (EDS). A thin gold coating was evaporated onto the surface of specimens for electrical conductivity before microscopic observations. The EDS analysis was used to provide the elemental distribution map of the coatings.

2.2.6. AFM

The surface roughness and topography of the $Ge_{1-x}C_x$ coatings were obtained by an atomic force microscopy (AFM, Danish Micro Engineering, Denmark) equipped with Dualscope C-21 controller and DME DS95-200E scanner. Images were provided in 15 μm/s scan rate and 29 nN force condition on the 10×10 μm^2 areas of the surface.