Dynamics of KrF Excimer Laser Plasma Plume Produced during Diamondlike Carbon Thin Film Preparation

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Abstract

Diamondlike carbon (DLC) thin films have an excellent combination of desirable properties such as hardness, high transparency, electrical insulation and low friction. We studied application of the DLC film as a protective coating for high temperature superconducting thin films. The DLC thin films were prepared by the KrF excimer laser deposition. We report spectroscopic measurements of the KrF laser plasma plume produced during the DLC thin film deposition. Optical emission provides information on the ablated species, their expansion velocities and the extent of ionization in the plasma plume. Neutral and ionic species such as H, C, C^+, CH, CH^+, C_2H, C_2H^+ were detected and changed depending on the processing conditions. It is showed that the properties of the DLC thin films is strongly affected by the laser plasma plume dynamics.

Introduction

Diamondlike carbon films have been attracting both intensive theoretical and experimental investigations due to their diamondlike properties such as hardness, highly optical transparency, chemically inert and high-resistivity[1-5]. Owing to their excellent properties, their application in the field of electronic devices have been expected. As a preparation method of thin films, the pulsed laser deposition (PLD) is rapidly proving to be a powerful method. The PLD has the advantages of high reproducibility, high deposition rate, of being a low temperature (around room temperature) process and easy to fabricate multilayer structures. The technique can be utilized not only to deposit materials which reproduce the stoichiometry and properties of the bulk target, but also to deposit

films with desired properties quite different from those of the starting material. Due to latter characteristics of the method, the PLD using a graphite carbon target seems to be promising way to prepare DLC thin films. And further, it may be easy to vary the physical and optical properties of DLC films by changing the deposition conditions in this method.

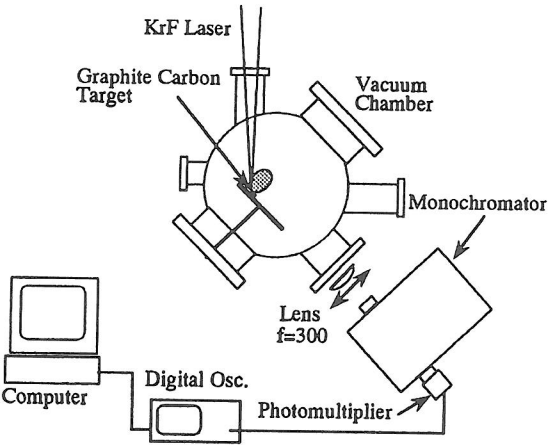


Fig. 1 Experimental setup.

We attempt to apply the DLC thin films as a protective coating layer on the high Tc superconducting (HTS) devices to improve their life time in operation[5]. In order to prepare DLC thin films with more favorable properties, we spectroscopically investigate a plasma plume from a graphite target ablated by a KrF laser. Optical emission provides information on the ablated species, their expansion velocities and the extent of ionization in the plasma plume. We also investigated the optical characteristics and the protective effect of the DLC films on the YBaCuO thin film deposited by the PLD.

Experimental

Figure 1 shows a schematic diagram of the PLD and optical measurement system used in this work. After the stainless steel high vacuum deposition chamber was evacuated by a compound turbo-molecular pump to a base pressure of 5×10^{-7} Torr, pure hydrogen gas was fed into the chamber using a mass flow controller. In the chamber a graphite carbon target (purity 99.99%) of 30 mm in diameter is mounted on a turning holder to avoid local drilling of the target by the laser. A KrF pulsed laser beam (Lambda Physik Model LPX305icc, maximum energy 850mJ, λ=248 nm, pulse duration of 20 ns) is introduced into the chamber through lenses and a fused quartz window. The laser energy for the DLC films deposition was 500 mJ/pulse and a repetition rate was 5 Hz or 10 Hz. The laser beam impinges on the target at an incident angle of 45° to its surface normal and has a spot size of 1.8×2.8 mm^2 at the target surface. The laser energy density at the target is estimated to be about 8 J/cm^2 taking account of optical loss. The laser-target interaction generates a bluish-white plasma plume which reaches to about 10 cm from the target in vacuum.

Spectral profiles (λ=400~800 nm) and a temporal behavior of the luminous plasma plume accompanying ablation under different ambient conditions were measured by

scanning a 250 mm-monochromator equipped with a photomultiplier and a digitizing oscilloscope. Emission light of the plasma plume at 10 mm or 20 mm from the target surface was collected by a f=300 mm convex lens and focused on the entrance slit of the monochromator.

In order to prepare the DLC thin films a quartz substrate was located at 50 mm apart from the target surface without heating in 200 mTorr hydrogen ambient gas. Transparency and the optical band gap of the film were measured by using a visible spectrophotometer.

Result and Discussion

Figure 2 shows the emission spectrum from the plasma plume in high vacuum. Spectra in vacuum are almost originated from mono-atomic carbons and carbon ions. The emission spectrum from plasma plume in 200 mTorr hydrogen atmosphere is shown in Fig. 3. In hydrogen atmosphere strong emission from neutral and ionic molecular species such as CH, C_2, C_2H, C_2H^+ were observed and spectral lines from carbon atoms were not identified. Molecules like CH, C_2, C_2H, C_2H^+ seem to be produced by the reaction in the gaseous phase. Identified spectral lines from carbon plasma plume in vacuum and hydrogen atmosphere are listed in Table 1. Wavelengths of observed molecular lines were slightly different (less than $\pm$ 1 nm) from tabulated ones.

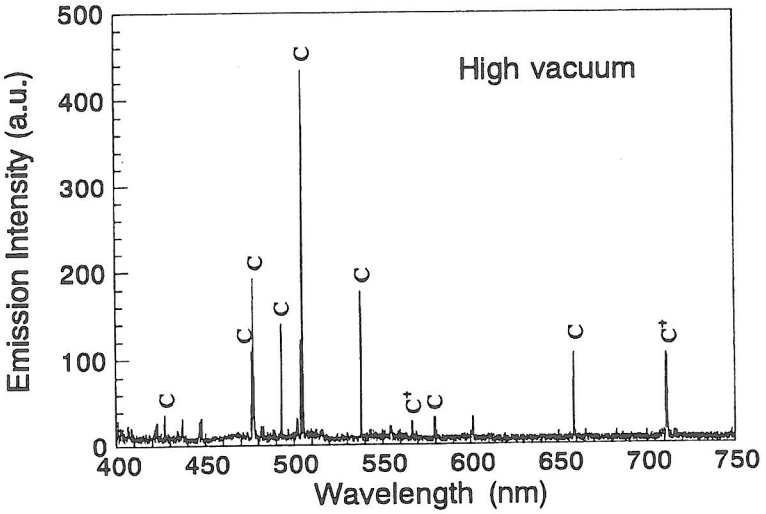


Fig. 2 Emission spectrum from carbon plasma plume in vacuum.

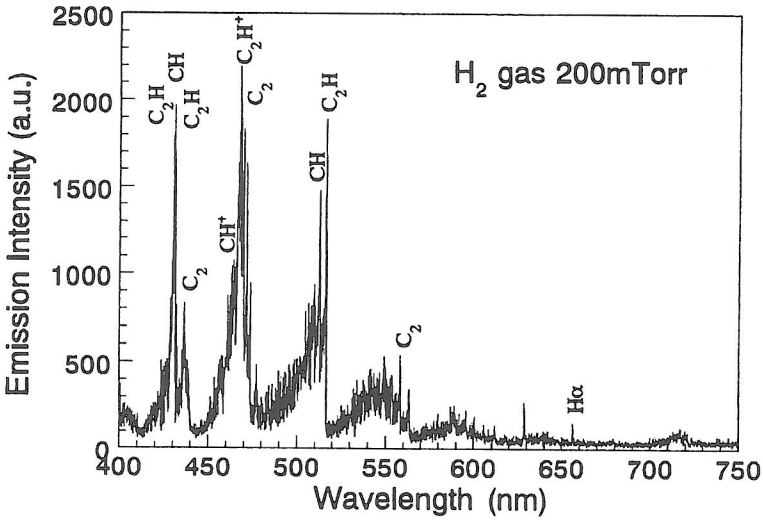


Fig. 3 Emission spectrum from carbon plasma plume in 200 mTorr H_2.

Figure 4 shows temporal changes of spectral intensity of CH (λ=430.6 nm) and C_2H^+ (λ=467.8 nm) at a distance of 10 mm and 20 mm from the target surface. These waveforms were measured by averaging 10 waveforms to improve a signal to noise ratio. At d=10 mm CH line appears about 0.4 μs after the laser incidence and slightly faster than C_2H^+, while at d=20 mm the waveform of CH line is broader than that of C_2H^+ line. Averaged velocities of CH and C_2H^+ between 10 mm and 20 mm from target are calculated

Table 1. Observed spectral lines in carbon plasma plume.

C	423.135	426.899	476.241	476.662	477.000	477.172
	477.587	481.733	493.200	503.905	504.166	505.212
	538.0242	579.351	580.117	658.775	711.85	
C^+	400.990	437.428	473.475	504.48	564.808	566.251
	609.862	711.236	711.513	711.945		
(C)	406.51	422.828	502.379			
CH	430.6	430.7	469.5	512.7		
CH^+	436.0	462.9				
C_2H	430.3	430.5	430.9	469.2		
C_2H^+	467.2					
C_2	436.2	516.0	558.0			

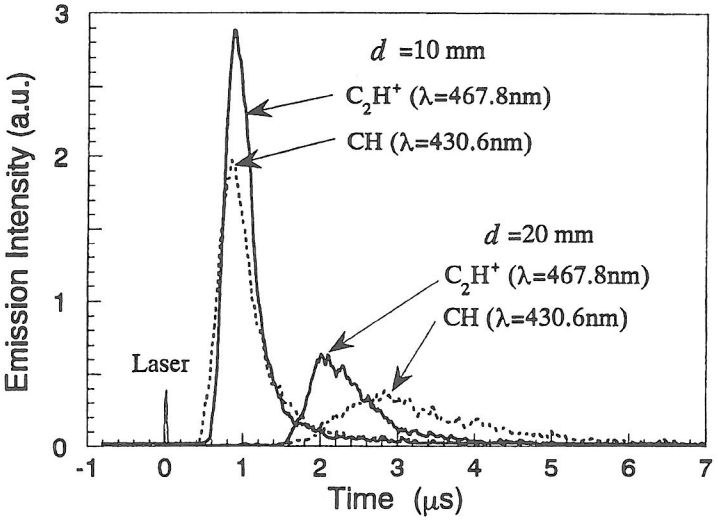
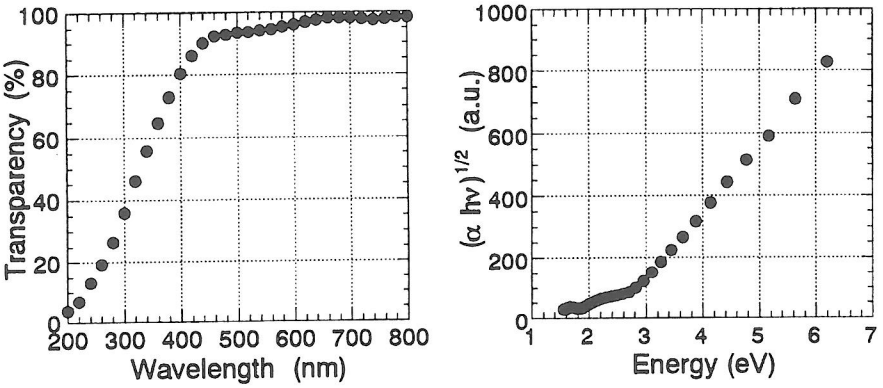


Fig. 4 Temporal change of emission intensity of CH and C_2H^+.

to be 5.7 x 10^3 m/s and 1.0 x 10^4 m/s, respectively. The difference of the emission signals between CH and C_2H^+ are due to their mass difference. CH molecules about half of C_2H^+ mass can easily gain and lose its kinetic energy than C_2H^+.

These results showed that the laser plasma plume dynamics, which depend on the ambient gas and its pressure and the distance from the target surface, strongly affects the



(a) Transparency of the film (b) Tauc plot of Fig.5 (a)

Fig. 5 Optical properties of the DLC thin film prepared in H_2.

properties of the DLC thin films.

The films deposited in the H_2 gas were amorphous hydrogenated carbon films with diamondlike properties. Transparency of the film is shown in Fig. 5 (a) and its Tauc plot is shown in Fig. 5 (b). The film is almost transparent in the visible region and has an optical band gap energy of 2.5 eV, which is about half of that of a diamond. The films deposited in high vacuum were opaque and had a smaller optical band gap energy and a larger hardness, and adhesion to the substrate was poor. Hydrogen atoms terminate dangling bonds of the amorphous carbon and are effective in improving some properties of the film.

The DLC film was deposited on a YBaCuO thin film to investigate the protective effect of the DLC film. Owing to the over deposition of the DLC film a critical temperature (Tc) of YBaCuO film was decreased a little but degradation of the Tc due to aging was not observed. It was found to be useful to protect the films in the humid atmosphere.

Conclusion

We have optically studied the dynamics of the plasma plume during preparation of DLC thin films by the PLD method. In depositions in the presence of hydrogen gas it was found that carbon atoms and ions emitted from the target react with ambient species and produce hydrocarbon molecules in the gas phase and their kinetic energy and densities change with both time and space. The protective coating of the YBaCuO films by the DLC layer seems to be appropriate in fabricating the oxide superconducting devices.

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