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Laser-induced graphitized periodic surface structure formed on tetrahedral amorphous carbon films

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ABSTRACT

Femtosecond laser-induced periodic surface structure (LIPSS), graphitization and swelling observed on ultra-hard, hydrogen-free tetrahedral amorphous carbon (ta-C) films are examined and compared with those on hydrogenated amorphous carbon (a-C:H) films, nitride films, and glassy carbon plates. The threshold fluence for LIPSS formation on ta-C is approximately twice as high as that for other specimens, and the LIPSS period Λ near the threshold is very fine at ca. 80 nm. Λ gradually increases with increasing fluence, and rapidly increases to ca. 600 nm at a high fluence. The ablation rate also increases rapidly at this fluence. In addition, ta-C and a-C:H are graphitized by irradiation and expand in volume. The surface layer of ta-C film changes to nanocrystalline graphite as the fluence increases and the crystallinity is improved; however, at higher fluence, the crystallinity deteriorates suddenly similar to that at low fluence. At high fluence, the rapid increase in Λ and the ablation rate, and the sudden deterioration in crystallinity are determined as common phenomena for these disordered carbons. LIPSS formation and swelling over a large area by scanned spot irradiation produces submicron height flat hills with conductivity and surface functionality on the insulating surface.

1. Introduction

Amorphous carbon films with a significant fraction of sp^3 bonds are referred to as diamond-like carbon (DLC) films and have been used in the industrial and medical-related fields in recent years [1–4]. DLC is classified into four types according to high or low sp^3 content and whether or not hydrogen is included. Amorphous carbon that does not contain hydrogen is classified into tetrahedral amorphous carbon with a high sp^3 content (ta-C) and amorphous carbon with a low sp^3 content (a-C), and those that contain hydrogen are classified into hydrogenated ta-C (ta-C:H) and hydrogenated a-C (a-C:H).

Among these, hydrogen-free ta-C films have extreme hardness and high density close to diamond, and exhibit excellent wear resistance, heat resistance and transparency. In the past, micron and/or sub-micron droplets generated during deposition of such films used to be a major problem, but with the use of advanced magnetic filtering systems, these problems have been overcome, and the latest films are smooth, dense, uniform and almost droplet-free [4]. These films have been recently used in the field of tribology such as for automobile parts, and their use has expanded and attracted significant attention [5,6].

Femtosecond (fs) lasers are capable of precision micromachining with extremely low thermal effects on difficult-to-process materials such as DLC, and fine laser-induced periodic surface structure (LIPSS) can be easily formed on the DLC surface [7,8]. The sp^3 sites in DLC film are also converted to sp^2 sites by fs-laser irradiation, so that DLC is modified to nanocrystalline graphite (nc-G) accompanied by an expansion in volume [9–13]. Fs-LIPSS has been increasingly reported as a surface design technology to optimize the frictional, wetting, optical, biological, and reactivity properties of a specimen surface [8]. Graphitization and swelling occur at the same time in DLC; therefore, it is expected to lead to new surface modification technologies.

In general, DLC films show high transmittance for infrared (IR) wavelengths [14–16], so research using ultraviolet (UV) nanosecond (ns) lasers has been reported to induce graphitization, swelling and improved frictional properties in DLC films [17–21]. Nistor et al. [17] reported TEM observations that indicated diamond particles of 2–7 nm size embedded in a low crystallinity graphite matrix of a-C:H films were formed at higher fluence, and that nc-G grows from 2 nm to 4 nm with increasing fluence. More recently, research on the effects of UV ns-laser irradiation on ta-C films with respect to graphitization and tribological

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