

Si doping enhances the thermal stability of diamond-like carbon through reductions in carbon-carbon bond length disorder

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ABSTRACT

Low thermal stability is a major limitation of diamond-like carbon (DLC) films, especially amorphous hydrogenated carbon (a-C:H) films, inhibiting their use in several applications. Adding silicon and oxygen to a-C:H increases thermal stability, but mechanisms for this increase are unknown. Reactive molecular dynamics (MD) simulations using the ReaxFF potential were performed on undoped a-C:H and a-C:H containing Si and O (a-C:H:Si:O). As in experiments, the simulated a-C:H:Si:O demonstrated increased thermal stability compared to a-C:H. Atomistic thermal degradation pathways were examined to understand the origins of the enhanced thermal stability of a-C:H:Si:O compared to a-C:H. The primary thermal degradation pathway in undoped a-C:H was the breaking of tensile strained C-C bonds resulting in a transformation of sp^3 to sp^2 -hybridized carbon. The presence of Si suppresses this mechanism by decreasing the frequency of occurrence of highly strained C-C bonds in the unannealed structure. This is due to the longer C-Si equilibrium bond length compared to C-C bonds, which allows the Si-doped films to accommodate higher structural disorder.

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1. Introduction

Carbon-based thin films have attracted wide research and technological interest due to their exceptional properties, such as high mechanical stiffness and strength, high hardness, low friction and wear, high electrical resistivity, chemical inertness, and extremely smooth surfaces [1–3]. These coatings have found uses in a wide variety of applications, particularly those demanding outstanding tribological performance, such as coatings for high-performance tools and automotive components, protective coatings for hard disks, microelectromechanical systems, and atomic force microscopy probes [4]. One of the most widely studied classes of carbon based films is diamond-like carbon (DLC), which refers to a broad class of materials including amorphous carbon (a-C) or hydrogenated amorphous carbon (a-C:H). The films can include both sp^2 and sp^3 hybridized carbon atoms [2].

DLC films are produced through direct ion beam processes and

various chemical vapor deposition methods, most commonly plasma-enhanced chemical vapor deposition (PECVD) [5]. The sp^2/sp^3 ratio and hydrogen content are dependent on the precursor gas compositions and the deposition parameters used (i.e., pressure, ion impingement energy, and surface power density at the substrate) [6]. Recently, advances in deposition techniques have allowed for the development of more complex DLC films by doping and alloying the DLC with metals, metalloids, or other elements from gaseous species such as Ti, B, S, Si, Cr, F, W, and N. These modified DLC films are capable of providing further improved mechanical, tribological, and thermal properties [7].

One critical application in which DLC films have been widely used is as the protective overcoat on magnetic storage media, such as hard disks [7–9]. Modern hard disks store data in a Co-based magnetic layer mounted on a substrate and covered with a hydrogenated amorphous carbon (a-C:H) overcoat and 1–2 monolayers of a lubricant film [8,10]. a-C:H is used since it forms a smooth, nanometer thick, and chemically inert film which protects the magnetic media against corrosion and mechanical contact with the read-write head [2]. In addition, the hard disk head is often coated with a tetrahedral amorphous carbon (ta-C) that is nearly hydrogen free [8], also to protect against wear and corrosion. H-free

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films are preferred on the head because their higher strength allows greater wear resistance at ultralow thickness (which is needed as the head is always in proximity to the disk), and their slightly higher roughness compared to a-C:H is tolerable on the head. However, to increase storage density there is interest in developing new heat-assisted magnetic recording (HAMR) disk drives, where a laser is used to locally heat the magnetic material during the recording process. This approach requires local temperatures of the head up to 300 °C, and of the disk of up to 500 °C during the recording process [11,12].

Unfortunately, current a-C:H films used for disk overcoats are not thermally stable, with degradation starting at temperatures as low as 150 °C [2,13]. The general trend at elevated temperature is increased wear, due to the transformation from sp^3 to sp^2 bonding, and oxidation of the film with carbon volatilization in aerobic environments. This has been reported at temperatures as low as 100 °C [14]. This presents a problem for the use of conventional a-C:H in the design of HAMR disk drives, and thus requires a new generation of protective films with enhanced thermo-oxidative stability to be developed [15]. The limited thermal stability of conventional hydrogenated amorphous carbon films is also a serious concern for other elevated temperature applications, such as protective coatings on components in car engines. One candidate for such a next-generation coating is silicon- and oxygen-containing a-C:H (a-C:H:Si:O). Such coatings have been produced commercially by PECVD using a siloxane precursor gas [1,16,17]. The use of a siloxane precursor is preferred to the use of silane gas, which is highly toxic and an explosion hazard, so silicon and oxygen are typically found together in commercial films [18]. In the literature it is proposed that a-C:H:Si:O consists of a diamond-like network of amorphous carbon and hydrogen (a-C:H) and a second amorphous silica network (a-Si:O) (see Fig. 1). These two networks are thought to be intermingled resulting in a purely amorphous structure [16,17].

Previous studies have shown that a-C:H:Si:O has significantly higher thermal stability than conventional a-C:H [1,20], however, no explanation has yet been provided for why the inclusion of silicon and oxygen, even at low atomic concentrations, results in such increases in thermal stability. An understanding of the mechanisms by which a-C:H:Si:O achieves higher thermal stability would be useful for film design and optimization.

2. Methods

Molecular dynamics (MD) simulations [21] are a valuable tool to gain insight into the atomic interactions that influence the structure/property relations in a-C:H:Si:O. By providing the ability to probe interactions between individual atoms, simulations can help to interpret experimental results and to overcome experimental challenges associated with studying amorphous thin films, such as

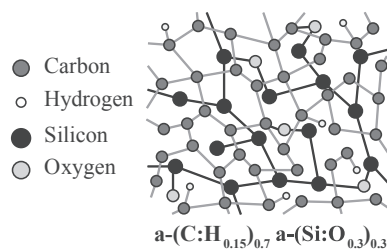


Fig. 1. Schematic diagram showing the structure of a-C:H:Si:O. The film is an amorphous structure consisting of a DLC network (a-C:H) with an interbonded Si and O. There is significant bonding between the two networks. Figure adapted from Refs. [17,19].

difficulty in accurately determining the carbon hybridization state [22,23]. Additionally, in the context of HAMR disk drives, the temperature pulses are on the order of 2 ns [12], a timescale that is experimentally challenging, but accessible in simulations. Several potentials have been used in the literature to model amorphous carbon to varying degrees of success, including AIREBO, EDIP, LCBOP, and ReaxFF [24]. However, for silicon- and oxygen-containing a-C:H the potential used must be parametrized for C, H, Si, and O, which significantly limits the choice of potential. For this work, the ReaxFF potential was used, with a Si/C/H/O force field developed by Newsome et al. [25,26]. ReaxFF makes use of bond order-dependent energy terms to describe reactive processes and allows for bond breaking and formation during simulations. The use of a reactive potential is essential to capture the chemical interactions that are central to the thermal degradation mechanisms. In addition, since the bonding configuration in amorphous materials is not known, a bond-order potential is necessary to determine a relaxed initial structure. The framework for the potential is designed to be very general and includes energy terms corresponding to covalent terms, Coulomb interactions, and non-bonding forces [25,27,28]. For this work the simulations were carried out using the molecular dynamics program LAMMPS [29,30].

The simulated a-C:H:Si:O samples' atomic composition and density were based on commercially available films purchased from Oerlikon Metco (Winterthur, Switzerland). The composition of these films (2 μm thickness) was measured by Rutherford backscattering spectrometry (RBS) and hydrogen forward scattering spectrometry (HFS), as well as by secondary ion mass spectroscopy (SIMS) performed by Evans Analytical Group (Sunnyvale, CA, USA). These techniques gave a consistent chemical composition of 57 ± 3 at.% C, 34 ± 3 at.% H, 6 ± 1 at.% Si, and 3 ± 1 at.% O. The film density was measured by X-ray reflectivity (XRR) as 1.8 ± 0.1 g/cm³, and $48 \pm 2\%$ of the C atoms were measured to be in the sp^2 hybridization state via near edge X-ray absorption fine structure (NEXAFS) spectroscopy measurements [31,32]. a-C:H films used in current hard disk drives were provided by HGST and used as control samples. The a-C:H films (20 nm thickness) have a hydrogen content of $26 \pm 3\%$ (measured by HFS, Evans Analytical Group), a density of $2.1 \pm 0.1\%$ (measured by XRR, HGST), and $51 \pm 1\%$ of the C atoms in the sp^2 hybridization state (measured by X-ray induced Auger electron spectroscopy) [22]. A comparison between the MD simulation results presented here and spectroscopic data acquired on a-C:H:Si:O and a-C:H will be reported elsewhere [31].

For annealing simulations, a-C:H and a-C:H:Si:O samples were produced following a liquid quenching procedure, which has been shown to be capable of reproducing the experimentally observed properties of amorphous carbon [33,34]. The goal of the liquid quenching procedure was to produce simulated samples that were matched to realistic values of composition, carbon hybridization, and density for a-C:H and a-C:H:Si:O films that exist and can be fabricated [22,31,35]. The initial simulation cell consisted of 2744 atoms selected to match the experimental atomic composition ([C] = 57%; [H] = 34%; [Si] = 6%; [O] = 3%) at a density of 2.3 g/cm³. Periodic boundary conditions were used in X, Y, and Z directions and the melting and quenching were carried out in the NVE ensemble. The time step for all simulations was 0.1 fs. The temperature was increased by velocity rescaling (using the LAMMPS temp/rescale command) to 6000 K, which was observed to be sufficient to melt the initial structure, and was maintained for 3 ps. The temperature was then reduced to 300 K over 1 ps by velocity rescaling following an exponential temperature profile, and the resulting structure was equilibrated at 300 K for 5 ps. It has been shown previously that short quenching times, on the order of 1 ps or less, are capable producing accurate a-C:H structures [24,36]. In fact, analysis of film deposition has shown sub-picosecond thermal

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