Nuclear Instruments and Methods in Physics Research B 394 (2017) 6–11

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Collision cascades enhanced hydrogen redistribution in cobalt implanted hydrogenated diamond-like carbon films

P. Gupta [a,b], H.-W. Becker [c], G.V.M. Williams [b], R. Hübner [d], K.-H. Heinig [d], A. Markwitz [a,b,*]

[a] National Isotope Centre, GNS Science, Lower Hutt, New Zealand
[b] The MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand
[c] RUBION, Ruhr-University Bochum, Germany
[d] Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, Germany

ARTICLE INFO

Article history:
Received 12 December 2016
Received in revised form 16 December 2016
Accepted 17 December 2016

Keywords:
Hydrogenated diamond-like carbon
Cobalt implantation
Room temperature
Hydrogen redistribution
Bimodal metal ion distribution
Collision cascades

ABSTRACT

Hydrogenated diamond-like carbon films produced by C_3H_6 deposition at 5 kV and implanted at room temperature with 30 keV Co atoms to 12 at.% show not only a bimodal distribution of Co atoms but also a massive redistribution of hydrogen in the films. Resonant nuclear reaction analysis was used to measure the hydrogen depth profiles (15N-method). Depletion of hydrogen near the surface was measured to be as low as 7 at.% followed by hydrogen accumulation from 27 to 35 at.%. A model is proposed considering the thermal energy deposited by collision cascade for thermal insulators. In this model, sufficient energy is provided for dissociated hydrogen to diffuse out of the sample from the surface and diffuse into the sample towards the interface which is however limited by the range of the incoming Co ions. At a hydrogen concentration of ~35 at.%, the concentration gradient of the mobile unbounded hydrogen atoms is neutralised effectively stopping diffusion towards the interface. The results point towards new routes of controlling the composition and distribution of elements at the nanoscale within a base matrix without using any heat treatment methods. Exploring these opportunities can lead to a new horizon of materials and device engineering needed for enabling advanced technologies and applications.

1. Introduction

Interaction of ions with matter is a subject of immense interest to the ion beam and material science community [1–3]. Several models have been developed that provide information on important information such as range and distribution of energetic ions in a matrix [1,4]. Various industry sectors including the semiconductor and high value manufacturing industries use these models to accurately calculate the concentration and profile of their implantation. However, new models are being developed to account for the thermal diffusion effects that arise due to the energy deposited during collision cascades [5]. In most cases, these effects are insignificant and can safely be ignored. In a few materials, especially in thermal insulators, diffusion may affect the implantation result by, for example, induced precipitation which can lead to unique distributions of the implanted atoms giving rise to interesting new properties and functionalities, for example, high magnetoresistance and condensed magnetism [6–8]. This is demonstrated in previous reports in which for example Cu and Ag implantation into thermal insulators such as silica and high purity silicon dioxide with implantation energy ranging from 60 to 260 keV led to bimodal distributions [9–11]. In one of our previous reports we presented bimodal distribution of Co in hydrogenated diamond-like carbon (DLC) for the first time [12]. The novel redistribution of implanted atoms is explained by using a model based on diffusion and precipitation processes enhanced by collision cascades. In this paper we report another significant new effect which can provide an even deeper insight into this process that has not been reported previously: a massive redistribution of hydrogen during ion implantation.

2. Materials and methods

2.1. Diamond-like carbon thin films

Diamond-like carbon is a material with significant fraction of its carbon bonded in sp^3 hybridisation [13]. The material is known for tits superb mechanical properties and is widely used in the coating industry for a wide variety of applications ranging from coating razor blades, to car engine parts, from mechanical tools to magnetic hard drives [13]. Recently, it was discovered that DLC may

---

* Corresponding author at: GNS Science, New Zealand.
E-mail address: a.markwitz@gns.cri.nz (A. Markwitz).

http://dx.doi.org/10.1016/j.nimb.2016.12.029
0168-583X/© 2016 Elsevier B.V. All rights reserved.

also be of interest for its magnetic and magneto-transport properties suggesting applications in magnetic semiconductors and magnetoresistance sensors and devices [6,14,15]. Transition metal ions can be implanted into DLC to enable novel magnetic functionality [6].

Hydrogenated diamond-like carbon films were deposited by mass selective ion beam deposition. Ion beam deposition allows control over precise film thickness and deposition temperature by preselecting the ion fluence and current [16,17]. This deposition process does not require high temperature and is ideal to deposit films on low melting point substrates as well as studying temperature dependent film properties. Mass selective ion beam deposition, in particular, offers accurate control over selection of ion species and ion energy. The DLC films were deposited with $C_3H_6^+$ ion species using butane as precursor gas to a fluence of $\sim 5 \times 10^{17}$ cm^{-2}. The selected fluence results in DLC films with thickness of about 100 nm. The deposition was carried out at 5 kV terminal voltage with a 2 μA cm^{-2} laterally scanned current in a sample chamber at high vacuum pressure ($\sim 1 \times 10^{-6}$ hPa). The molecular ion beam dissociates upon impact. The deposition energy is distributed among the dissociated atoms based on their mass [17]. The detailed energy distribution and the respective range and straggling of carbon and hydrogen atoms in DLC matrix and silicon calculated by Stopping Range of Ions in Matter (SRIM) [18] are given in Table 1.

2.2. Ion implantation

Cobalt ions were implanted at GNS Science using the 40 kV terminal, 90° analysing magnet and electrostatic double quadrupole and scanner ion implanter [19,20]. The terminal voltage was set to 30 kV. A Penning sputter ion source was used to generate the Co ions. In the source, Co ions were sputtered from electrically conductive solid Co targets inside the ion source with the use of neon gas. The sputtered ions were passed onto a 90° electromagnet that separates ions based on their energy, mass and charge. The ion beam was directed towards the sample chamber with the use of electrostatic steerers and lenses. The implantation was carried out at an ion current density of ~ 5 μA cm^{-2} to avoid any bulk heating effects during implantation. The fluence was varied from 1 to 10×10^{16} cm^{-2} and the sample chamber was evacuated to a vacuum pressure of $<1 \times 10^{-7}$ hPa.

2.3. Ion beam analysis

Rutherford backscattering spectrometry was used to measure the concentration and profile of Co implanted into DLC films. The RBS spectra were measured using a 2 MeV He^+ ion beam from the 3 MV HVEC single ended Van de Graaff accelerator at GNS Science. A solid state silicon surface barrier detector was used to detect the backscattered He particles. The detector was placed at an angle of 165° to the incident beam in the sample chamber and was covered by a vertical slit aperture of 1 mm cross-section to ensure high angular resolution. A low ion current of 10–20 nA was used to measure the implanted samples non-destructively. Data for each sample was collected to a charge of 20 μC to provide good statistical accuracy.

In order to obtain hydrogen profiles of the as-deposited and implanted DLC films, the samples were measured by Nuclear Resonant Reaction Analysis (NRRA) using a ^{15}N ion beam generated by the 4 MV tandem accelerator at RUBION, Bochum. The measurement is based on the nuclear reaction $15N + {}^1H \rightarrow {}^{12}C + {}^4He + \gamma$. At the resonance energy of 6.385 MeV, ^{15}N isotopes react with hydrogen resulting in gamma ray emission at 4.43 MeV. A 12 in. × 12 in. NaI(Tl) bore hole detector was used to detect and record the gamma rays, which are proportional to the hydrogen content in the material. The beam current was limited to 5 nA to reduce loss of hydrogen from the films during the measurements. The data was collected in the energy range of 6.35–6.65 MeV. The resolution of the beam energy is 15 keV. As the energy of the beam is increased, the resonant reaction occurs in a deeper region in proportion with the increase in beam energy. The samples were measured is steps of 6 keV. At each step, data was collected to a charge count of 100 nC. The standard used for the measurement is an amorphous silicon layer that contains 12.5 at.% of hydrogen. The hydrogen concentration of the samples were calculated in comparison with the standard [19].

2.4. Transmission electron microscopy

To locally analyse the hydrogenated DLC films in the as-deposited state and after Co ion implantation, transmission electron microscopy (TEM) investigations were carried out using an image C_s-corrected Titan 80–300 microscope (FEI) operated at an accelerating voltage of 300 kV. In particular, cross-sectional bright-field TEM (BF-TEM) micrographs were taken to characterize morphology and microstructure of the DLC films. Prior to TEM analysis, the specimen mounted in a double-tilt analytical holder was placed for 10 s into a Model 1020 Plasma Cleaner (Fischione) to remove organic contamination. TEM lamella preparation was done by in situ lift-out using a Zeiss Crossbeam NVision 40 system. To protect the surface of the DLC film, a platinum cap layer was deposited beginning with electron beam assisted and subsequently followed by Ga focused ion beam (FIB) assisted precursor decomposition. Afterwards, the TEM lamella was prepared using a 30 keV Ga FIB with adapted currents. Its transfer to a 3-post copper lift-out grid (Omniprobe) was done with a Kleindiek micromanipulator. To minimize sidewall damage, Ga ions with only 5 keV energy were used for final thinning of the TEM lamella to electron transparency.

3. Results and discussion

Fig. 1 shows cross-sectional BF-TEM micrographs of as-deposited (a) and Co-implanted DLC films (b).

As can be seen, the surface of the films is covered by a platinum contrast and protection layer deposited during TEM lamella preparation. The nanometre-smooth amorphous DLC films are shown to be uniform throughout the thickness, except at the DLC-Si interface. There, an interfacial layer (<10 nm) with increased mass contrast, arising from the mixing of carbon and hydrogen with the

Table 1
Energy distribution and the respective range and straggling of carbon and hydrogen atoms in DLC matrix and silicon.

S.No	Ion	Energy (eV)	In DLC		In silicon	
			Range (nm)	Straggling (nm)	Range (nm)	Straggling (nm)
1	H	119	3.4	3.6	3.1	4.7
2	C	1428	6.8	3.2	6.6	5
3	Co	30,000	34.6	7.6	29.1	10.7