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Molecular carbon nitride ion beams for enhanced corrosion resistance of stainless steel

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ABSTRACT

A novel approach is presented for molecular carbon nitride beams to coat stainless surfaces steel using conventional safe feeder gases and electrically conductive sputter targets for surface engineering with ion implantation technology. GNS Science's Penning type ion sources take advantage of the breaking up of ion species in the plasma to assemble novel combinations of ion species. To test this phenomenon for carbon nitride, mixtures of gases and sputter targets were used to probe for CN^+ ions for simultaneous implantation into stainless steel. Results from mass analysed ion beams show that CN^+ and a variety of other ion species such as CNH^+ can be produced successfully. Preliminary measurements show that the corrosion resistance of stainless steel surfaces increased sharply when implanting CN^+ at 30 keV compared to reference samples, which is interesting from an application point of view in which improved corrosion resistance, surface engineering and short processing time of stainless steel is required. The results are also interesting for novel research in carbon-based mesoporous materials for energy storage applications and as electrode materials for electrochemical capacitors, because of their high surface area, electrical conductivity, chemical stability and low cost.

1. Introduction

Carbon nitride is a new class of carbon based materials believed to be harder than diamond and researched recently for the potential application in photo catalysis and anti-corrosion [1]. The preparation techniques such as atmospheric pressure chemical processing, ion beam deposition, laser processing, chemical vapour deposition and sputtering techniques including ion beam deposition have been employed to prepare carbon nitride materials with different structures [2]. Significant literature exists around single carbon and nitrogen ion implantation into stainless steel and their benefits. See for example Blawert et al. and Samandi [3,4]. Molecular ion beams can lead to significant new materials properties as described for example by Shi [5]. Focus on graphitic carbon nitride C_3N_4 is due to most interesting properties that vary with structure and morphology [3]. They can be used for example as metal-free catalysts, super hard materials and as efficient photo catalyst [6–8].

This research is based on research in molecular ion beam based diamond-like carbon (DLC) coatings. At GNS Science are have developed 'high energy' molecular ion deposition techniques for DLC research [9–12]. Being able to use hydro-carbon ion beams enables the 'implantation/deposition' of carbon and hydrogen atoms simultaneously producing diamond-like carbon films with high elasticity, high hardness, low thermal conductivity and varying sp2/sp3 content [10,11]. They show great promise of new diamond-like carbon films for applications in magnetic field sensor when implanted with magnetic ions [13–15].

The aim of this work is to demonstrate how molecular ion beams from Penning ion source can be generated to develop carbon nitride microstructures on metal substrates.

2. Experimental

Ion implantation is a standard technique at GNS Science available to modify surfaces of solid materials with positive ion beams from 5 to more than 100 kV [16]. Three ion implanters have been developed at GNS Science over the past 15 years to enable implantation of any element of the periodic table. To date, positively charged ion beams have been produced from 55 elements from hydrogen to bismuth with three different Penning ion sources

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types; (1) gas ion source for high current ions required from the gas phase, (2) sputter ion source for high current ion beams from solid conductive sputter targets, and (3) oven ion source for specific elements such as sulphur that have a low melting point. The sputter source also works with pressed pellets enabling production of electrically non-conductive materials when mixed with conductive powder. Although the implanters at GNS Science offer already a wide energy range, often multiple charged ions are used to increase the penetration depth. As a rule of thumb, Penning ion sources produce 100% 1+, 10% 2+, 1% 3+ ion beams and so forth. Molecules are 'disassembled and assembled' in the plasma in the source extending the range of ion species further to new exotic molecular ion species, such as HCN^+ as described later. For this research, the 40 keV mass selected ion implanter dubbed 'the industrial implanter' was used. This system consists of a Penning ion source coupled to an Einzel lens, a four plate electrostatic steerer (±3000 V) at the 40 cm electro magnet. The beamline consists of a pair or electrostatic quadrupole lenses (±5000 V), a pair of slits to improve the mass resolution, a 4-plate bipolar electrostatic steerer mounted straight after the magnet (±800 V), a Faraday cup to start stop the implantation process, an electrostatic 2-axis scanner (±2000 V) with adjustable voltage and beam offset, both in horizontal and vertical direction. The implanter has two pairs of slits in the beam line. The first pair of slits was set to 1 mm gap horizontal and 4 mm gap vertical. The second horizontal slit was set to 10 mm gap. This setup results in excellent mass resolution of 0.5 amu and less in the mass region around the mass 26. Reproducibility of the measurements was confirmed by repeatedly sweeping the magnetic field of the magnet in the mass region of 20 to 32 amu and by measuring repeat current values at mass 26 for CN^+.

The target chamber has a load lock stage and operates at 5×10^{-8} hPa during implantation using a combination of turbomolecular pumps and liquid nitrogen cooling of a cold shield. The ion current is monitored by the charge integrator that is also used to pre-set the semi-automatic implantation process. Samples of 15 × 15 mm in size were implanted at room temperature. Apertures of 10 mm in diameter were used in front of the samples to restrict the implantation area and to enable implanted/unimplanted areas on the same target.

RBS was used to probe the surface of the implanted samples. A 2.0 MeV ion beam was used for the experiments [17]. The surface barrier detector was placed at 165°. Apertures in the beam line and close to the target were set to 1 mm resulting in an energy resolution of 20 keV FWHM.

3. Results and discussion

A large variety of ion species can be produced by the Penning ion source using a gas mixture of CO and N_2. Details are given in Table 1. Note the current values given have been recorded during the testing only. Higher currents were used for the experiments using improved implanter settings, sputtering of carbon by nitrogen in the ion source and be carefully tuning the implanter at selected energy and mass. Fig. 1 shows a picture of the GNS Science Penning ion source used for the experiments.

As can be seen, the majority of the ion current is produced for N_2 and CO molecular ion species. This is expected due to use of N_2 and CO feeder gas. CN^+ ions are produced close to 1%. Exotic molecular ions such as H_2O^+, COH^+ and CNH^+ are produced as well. The latter is surprisingly present at 8.5% of the ion beam current indicating a preferred bonding of H to CN in the plasma compared to simply producing a CN^+ ion beam. The presence of hydrogen in the beam is typical for ion implanters in which metal tubing is used and pumping time between different experiments is usually insignificant. This is usually not important for experiments because of the mass resolution of the system in which unwanted ion beams are filtered out by the magnetic field and slits. The magnetic field scan shows that CN^+ ions are actually produced in the plasma. Note data were recorded with 10 mm slit settings, horizontally and vertically. Steel and titanium target were implanted to 1×10^{17} cm^{-2}, respectively. The ion current was optimised for the implantations and set to ≤ 5 μA to avoid any thermal sample heating during the implantation process.

Fig. 2 shows a representative RBS spectrum of a CN^+ implanted steel sample recorded in the channel region of 600–1000.

As can be seen from the RBS spectrum in Fig. 2, the surface region of the implanted stainless steel coupon reflects the implantation of carbon and nitrogen species. The spectrum was analysed with RUMP software [18]. T-DYN calculations provided elemental depth profiles considering sputtering and atomic rearrangement during the calculations [19]. The composition of the surface layer with a thickness of $550 \pm 25 \times 10^{15}$ cm^{-2} was simulated by RUMP to contain Fe 78% and C and N 22%. This data was compared with T-DYN calculations using the implantation parameters as input parameters considering the ion beam hit the surface perpendicular and the stainless steel density of 7.6 g cm^{-3}. The T-DYN calculation is shown in the inset in Fig. 2. According to T-DYN calculations, the final mean projected range is 44.84 nm, sputtering yield is 0.7 and backscattering per ion is 0.06. The CN profile extends to the surface. The maximum range of CN atoms is 100 nm as shown in the insert in Fig. 1. Both, the measurement and the calculation are in good agreement in terms of peak concentration of implanted atoms and overall depth profile of atoms considering the energy resolution of the RBS measurement of FWHM = 20 keV.

Series of samples were implanted to the CN concentration of 20% at which point the ternary FeCN phase diagram has a eutectic point [20]. CN was implanted to the ratio of 1:1 to achieve a graphitic state [21]. Our ion implantation process is regarded as a 'cold' process due to the thermal conductivity of 79.5 W mK^{-1}. Stainless steel and iron are good thermal conductors and therefore the implantation conditions reported in the publication are regarded as surface engineering at room temperature. Note, temperature ranges from 1250 to 1800 °C are typically used to produce FeCN compounds [24]. Hence, chemical bonding during the implantation process is limited but maybe enhanced if C and N are implanted simultaneously from a single ion. This is in contrast to hydrogenated DLC in which not only bonds are created during the implantation but also atomic diffusion occurs of the length of 10 nm and which is coupled with Oswald ripening [14,15]. In this case the thermal conductivity of the material is sufficiently low (less than 1 W mK^{-1}) to allow these processes to happen, even at room temperature [22].

The samples were further analysed with atomic force microscopy to probe for alterations at the surface due to the ion bombardment. A system from Nanosurf was used for the measurements that routinely images the surface of smooth materials to the 0.1 nm resolution [23]. The data were analysed and average values are reported. For the statistical analysis, a surface area of 100 × 100 μm was analysed. The average surface roughness is measured to be between 20 and 25 nm for both, implanted and non-implanted regions. Fig. 3 shows three representative AFM scans that were measured in the implanted region. As can be seen, the overall roughness of the surface is about 0.1 μm. It is concluded that the implantation did not significantly influence the surface roughness in the implanted area.

This is in agreement with preliminary water contact measurements which were performed to probe for hydrophilicity. The setup allows for water contact measurements between 0 and 90° tilt angle. The measurements showed that the contact angle varied between 65 and 72°. The implantation may have slightly increased

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