Modification of surface properties of silicon micro-molds by nitrogen and silicon doped diamond-like carbon coatings deposited with magnetron co-sputtering

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ABSTRACT
This paper investigated the effect of nitrogen gas (N2) flow rate on the structural, mechanical and tribological properties of nitrogen (N) and silicon (Si) doped diamond-like carbon (Si:DLC:N) coatings deposited on Si micro-molds via magnetron co-sputtering deposition with respect to the bare Si molds. Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) showed that the amount of sp2 bonds and cluster size of the coatings increased with the increase in N2 flow rate. It was noticed that the surface roughness (Rq) of the Si:DLC:N coated molds increased from about 3.8 to 7.8 nm with increased nitrogen flow rate from 5 × 10⁻⁶ to 25 × 10⁻⁶ m³/min, but the variation of roughness between the coated and uncoated Si molds was not significant. Ethylene glycol and deionized (DI) water were used to measure their contact angles with the mold surfaces, which were used to evaluate the surface energy of the molds. The total surface energy of the coated molds increased from about 38.2 ± 2.3 to 66.5 ± 2.3 mN/m with the increase in N2 flow rate from 5 × 10⁻⁶ to 25 × 10⁻⁶ m³/min. The coefficient of friction (COF) of the coated molds decreased with increased N2 flow rate.

1. Introduction
Hot embossing is one of the most common patterning techniques for high throughput and low cost polymeric devices. However, high adhesion and friction can cause a high demolding stress during a hot embossing operation, which leads to the distortions of microstructures [1].

Diamond-like carbon (DLC) is a metastable amorphous carbon with superior tribological and mechanical properties [2], which make it suitable for the hot embossing process. However, a few disadvantages of DLC coatings, such as high internal stress, poor adhesion to substrates, and limited coating thickness, derail certain applications [3,4]. Silicon and nitrogen have been used to dope DLC coatings to address the above issues [5].

This work aims to improve the surface properties of Si micro-molds by means of N and Si doped DLC coatings.

2. Experimental details
Si:DLC:N coatings were deposited on Si micro-molds using magnetron co-sputtering under a vacuum pressure of about 0.4 Pa and a substrate bias of ~90 V with graphite (99.99% C) and Si (99.99% Si) targets of 4 inch in diameter under a DC power of 650 W and an RF power of 25 W, respectively. The Ar gas flow rate was kept constant at about 50 × 10⁻⁶ m³/min. Five different Si:DLC:N coatings were produced with varying N2 flow rates starting from 5 × 10⁻⁶ m³/min up to 25 × 10⁻⁶ m³/min with a constant increment of 5 × 10⁻⁶ m³/min up to 25 × 10⁻⁶ m³/min N2, which were designated as N5, N10, N15, N20 and N25, respectively.

The bonding structure of the coatings was determined with Raman spectroscopy using a He−Ne ion laser of 633 nm in wavelength and XPS (Kartos Axis Ultra) using a monochromatic Al Kα excitation of 1486.71 eV with pass energies of 160 and 40 eV for wide and detail scans respectively. The roughness of the molds surface was measured by using atomic force microscopy with a Si3N4 cantilever in tapping mode. The hardness of the coated mold surfaces was measured by nanoindentation with allowable drift rate and frequency of 0.1 nm/s and 45 Hz, respectively. A ball-on-disk micro-tribometer (CSM) was used to study the tribological behavior of the Si:DLC:N coated and bare Si molds. A SiC ball of 6 mm in diameter was slid along a track of 1 mm in radius at...
a speed of $5 \times 10^{-2}$ m/s and a normal load of 1 N. Numbers of laps for coefficient of friction and wear were 250 and 5000, respectively. SEM and confocal microscopy were used to study the wear profiles. Hot embossing experiments were carried out to study the performance of the coated and uncoated micro-molds.

The surface tensions of the micro-molds were determined by means of contact angle method. The relations among surface tension and its dispersive and polar components, and contact angle are expressed in Equations (1)–(4) [6,7].

$$\gamma_{sl} = \gamma_{sl} + \gamma_{lv} \cos \theta$$ \hspace{1cm} (1)

$$\gamma_{sv} = \gamma_{sl}^d + \gamma_{lv}^p$$ \hspace{1cm} (2)

$$\gamma_{lp} = \gamma_{lp}^d + \gamma_{lp}^p$$ \hspace{1cm} (3)

$$\gamma_{sl} = \gamma_{sl}^d + \gamma_{sl}^p$$ \hspace{1cm} (4)

where $\gamma$ is the surface tension, superscripts $d$ and $p$ respectively refer to the dispersive and polar components, subscripts $sv$, $lv$ and $sl$ respectively refer to the solid-vapor, liquid-vapor and solid–liquid interfaces and $\theta$ is the measured contact angle.

The dispersive and polar components of surface tensions are related by Equations (5) & (6) [7].

$$\gamma_{sl}^d = \gamma_{sl}^d + \gamma_{lp}^d - 2\left(\gamma_{sl}^d - \gamma_{lp}^d\right)^{1/2}$$ \hspace{1cm} (5)

$$\gamma_{sl}^p = \gamma_{sl}^p + \gamma_{lp}^p - 2\left(\gamma_{sl}^p - \gamma_{lp}^p\right)^{1/2}$$ \hspace{1cm} (6)

All above equations are correlated through Equation (7).

$$(1 + \cos \theta)\left(\gamma_{lp}^d + \gamma_{lp}^d\right)^{1/2} = 2\left(\gamma_{sl}^d - \gamma_{lp}^d\right)^{1/2} + 2\left(\gamma_{sl}^p - \gamma_{lp}^p\right)^{1/2}$$ \hspace{1cm} (7)

The dispersive and polar components ($\gamma_{sl}^d$ & $\gamma_{sl}^p$) of solid surface tensions are calculated by measuring water and ethylene glycol contact angles with respect to their known dispersive and polar components [8].

3. Results and discussion

In Fig 1, the Si:DLC:N coatings exhibit two broad Raman peaks at about 1350 and 1550 cm$^{-1}$ related to D and G peaks, respectively. The Raman spectra show that the G peak shifts toward higher positions with the increase in $N_2$ flow rate as indicated by the dotted line in Fig. 1. It is also observed that the intensity ratio ($I_D/I_G$) shifts to higher values with higher $N_2$ flow rates. All these results imply that graphitization and cluster size of the Si:DLC:N coatings increase with increased $N_2$ flow rate [9–11]. Fig. 2 shows the XPS C 1 s bond of the N15 coating and the inset in the figure illustrates that the C–C $sp^2$ and $sp^3$ bonds increase and decrease with the increase in $N_2$ flow rate, respectively.

The root-mean-square surface roughness ($R_q$) values of the Si:DLC:N coated and bare Si molds are in the order of N25 (7.8 nm) > N20 (5.4 nm) > N15 (4.9 nm) > N10 (4.7 nm) > N5 (3.8 nm) > bare Si (1.1 nm). A higher N content in a DLC coating can promote the $sp^2$ bonding, which lowers the stress and increases the graphitic cluster size in the coatings, leading to a higher surface roughness of the coating [11].

Fig. 3 shows the load vs. penetration depth profiles of the Si:DLC:N coated molds, where the hardness decreases with increased $N_2$ flow rate due to decreased $sp^3$ content in the coatings.

The bare Si micro-mold shows a higher coefficient of friction than all the Si:DLC:N coated molds. Graphite-like $sp^2$ bonds can act as a solid lubricant and decrease the friction coefficient. Therefore, a higher $N_2$ flow rate lowers the friction coefficient as it promotes a higher fraction of $sp^2$ bonds. The N20 sample shows a lowest friction coefficient of about 0.2 that is almost similar to that of the N25 as shown in Fig. 4.

Fig. 5 shows the wear depths and widths of the Si:DLC:N coated and bare Si molds as a function of $N_2$ flow rate and the inset depicts

![Figure 1: Raman spectra of (a) N5, (b) N10, (c) N15, (d) N20 and (e) N25.](image)

![Figure 2: Deconvoluted C 1 s peak of N15. The inset illustrates the changes of $sp^2$ and $sp^3$ with respect to $N_2$ flow rate.](image)

![Figure 3: Load-displacement curves from nanoindentation tests of various Si:DLC:N coatings.](image)
the wear track of the N10 sample. The bare Si mold exhibits larger wear depth and width than all the Si:DLC:N coated molds. The depths decrease with the increase in N2 flow rate up to $15 \times 10^{-6}$ m$^3$/min and then increase with further increase in N2 flow rate. An increase in sp$^2$ amount in the coatings lowers the friction coefficient, which decreases the wear width and depth of the coatings but the hardness of the coatings is also reduced, which causes a further increase in wear width and depth (for example, see N20 and N25 coatings).

Fig. 6 shows that N2 flow rate has a great influence on the surface contact angle and surface tension of the Si:DLC:N coatings. The surface tension of the Si:DLC:N coatings increases with the increased N content in the coatings, which is due to the increased polar component. From Fig. 6, a highest surface tension of about 66.5 mN/m is observed for the N25 sample, while a smallest surface tension of around 38.2 mN/m is observed for the N5 one.

The most critical step in hot embossing process is demolding, as the Si molds are easily broken at this stage due to the higher friction and adhesion forces occurring between the Si mold and work part surfaces in contact. The average lifetime of the bare Si micro-molds is about two times higher. It is interesting to note that the Si:DLC:N coatings can significantly enhance the surface properties of the Si micro-molds by lowering the friction coefficient and surface tension of the molds, which prolongs the lifetime of the molds by up to eight times.

4. Conclusion

Raman and XPS analyses of Si:DLC:N coatings showed that an increase N2 flow rate promoted the formation of graphite-like bonds in the coatings. Higher N content in the Si:DLC:N coatings also induced higher surface roughness of the coatings. It was observed that N25 had the highest surface roughness of about 7.8 nm. The friction coefficient and hardness of the Si:DLC:N coatings decreased with the increase in N2 flow rate and N20 coatings showed the lowest friction coefficient of about 0.2 measured on the samples. The N25 coating was the most hydrophilic and had a highest surface tension of about 66.5 mN/m among the coatings used in this study. The Si:DLC:N coatings could prolong the lifetime of the Si micro-molds by up to eight times.

References