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Graphene-coated Si mold for precision glass optics molding

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Despite many attractive properties and well-developed micro/nano manufacturing technologies based on silicon (Si) wafers, severe adhesions between Si and glass at high temperature have limited its application as a mold material in precision glass molding. In this Letter, a coating using carbide-bonded graphene is introduced to build nonstick Si molds for glass molding. The coating has extraordinary mechanical properties and can effectively prevent Si-glass adhesion under high temperature. We demonstrated fabrications of a Fresnel lens and glass parts with micrometer pillars using graphene-coated Si molds. This newly developed process enables the use of Si as a mold material to fabricate sophisticated structures with high-precision dimensions that was not previously available. This technology will greatly improve precision glass molding process and allow high-precision low-cost glass optics to be manufactured in large quantity. © 2013 Optical Society of America

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Silicon is one of the most widely used materials in microfabrication because of its material properties, available processing methods, and low manufacturing cost [1]. Various features and structures have been fabricated on Si substrates, such as microlens arrays [2] and optical gratings [3]. On the other hand, these types of features are often encountered in precision glass molding, a net-shaping process for glass optics fabrication by replicating optical features from precision molds to glass at elevated temperature [4–6]. However, Si cannot be used directly as mold material due to severe adhesions between Si and glass. The adhesions are either caused by anodic bonding or chemical bonding at elevated temperature [7].

A few attempts have been made to use silicon molds for glass molding. For example, Albero et al. demonstrated the molding of glass microarrays on a Si mold, which, however, had to be completely etched after molding to release the glass lens array [8]. This Si-sacrifice molding method consisted of multiple steps and the Si mold could only be used once; thus, it is not an economical approach. Hirai et al. used a Si3N4/SiO2/Si mold for imprinting fine patterns to glass surfaces, but the mold had limited feature depth because it was created on a thin layer of SiO2 instead of directly on the Si substrate [9]. Chen et al. fabricated a micromachined silicon mold for a Fresnel lens glass molding [10]. However, the process was limited to low glass-transition temperature (Tg) glasses, therefore the molded optics had poorer quality as compared to regular glass.

In this research, we developed a technique that can be used to prevent adhesions between Si molds and the molded glass optics by utilizing a thin layer of carbide-bonded graphene, a two-dimensional material with extraordinary mechanical properties [11]. The building of a strong graphene coating as a protective layer on silicon substrates [12] provides the surface with a unique combination of many advantages, such as high thermal conductivity, high hardness, and low surface friction. This newly developed technology makes it possible to use micro/nano patterned Si wafers for high volume precision glass optics fabrication, thus resulting in a process with low manufacturing cost. Although other materials, such as glassy carbon, chemical vapor deposition (CVD) diamond, and nitride ceramics were also used as mold materials [13,14], most of these materials cannot match Si in terms of versatility of micro/nanoscale fabrication, material availability, and manufacturing cost [1].

In this Letter, we demonstrated precision molding of glass micro-optics with graphene-coated Si molds. As described below, the coating process requires the heating of high-temperature silicone rubber, a piece of GP-SiO2H nanopaper [15], as well as Si substrates inside a quartz tube. First, the quartz tube was heated in vacuum from room temperature to 500°C in 30 min. Vacuum was applied to remove air in the system. Then vacuum line was turned off and the sealed system was further heated from 500°C to 1000°C in 20 min. At elevated temperature, silicone rubber was thermally degraded into silicon or silicon oxides radicals. At the same time, benzene sulfonic acid groups in the nanopaper were thermally decomposed to form gases like SO2 and CO2. Because of the formation of gas bubbles inside the nanopaper layers, graphene sheets exfoliated and eventually flew away from the nanopaper. Reactive sites like carbon radicals were formed at the edge of graphene or on the basal plane, possibly at which the functional groups were bonded before degradation [12]. Third, the system was kept at 1000°C for 30 min. At this temperature, silicon substrate surface was activated to produce −Si and −SiO active groups. As the vacuum was released due to formed gases, nitrogen gas was introduced to maintain an atmospheric pressure. As illustrated in Fig. 1(a), the exfoliated graphene nanosheets were deposited to Si surface and reacted with thermally activated Si, SiO2, or OSiO-radicals, eventually built robust C–Si and C–O–Si bonds between the graphene nanosheets and the substrate and also between neighboring graphene
Finally, the system was naturally cooled to room temperature. The coated sample was washed with water and acetone to remove ash on the coated surface, followed by drying in vacuum oven at 100°C overnight. The surface roughness of an uncoated Si wafer and a coated Si wafer were measured using a white light optical profilometer (Wyko, NT9100). As shown in Figs. 1(b) and 1(c), no notable differences were found in surface roughness between the uncoated and coated Si wafers.

The carbide-bonded graphene coatings on silicon substrates provide a unique combination of many attractive properties for glass molding. Graphene is an excellent thermal conductor that enhances heat transfer from the Si substrate to glass and can also help generate a uniform temperature distribution during glass molding. The analysis and testing of the thermal conductivity of this carbide-bonded graphene coating will be discussed in a separate paper. The friction coefficient of the graphene coating is found to be only 0.029, which is more than 60% lower than that of a silicon wafer (0.076) \[12\]. The low friction coefficient can improve the filling ability of glass into small features on molds. The graphene-coated Si mold has also greatly increased Young’s modulus and hardness that can minimize the wear of molds during compression molding. In addition, a robust antiscratching capability is also an indicator of a long mold life \[12\].

In order to test the coatings on nonflat surfaces, a Si mold with microwells was fabricated using standard photolithography and inductively coupled plasma-reactive ion etching (RIE) method. A thin film graphene coating was applied to the surface of the Si mold. The surface profile of the coated Si mold, which was measured using a Wyko NT9100 optical profilometer, is shown in Fig. 3(a) and the scanning electron microscope (SEM) image of the mold is shown in Fig. 3(b). Each microwell has a width of 11 μm and average depth of 1.5 μm.

A glass blank was molded on the graphene-coated mold. The replicated features on glass were scanned and shown in Fig. 3(c). In this figure, highly uniformed micrometer pillars were formed on the glass surface with an average height of 1.5 μm, which matches the dimensions of the microwells on the Si mold. This demonstrated that high-precision microfeatures can be successfully transferred to glass surfaces using this method.

The good surface finish on the molded glass indicated that it is possible to fabricate high-precision glass optics with graphene-coated Si molds. As a proof-of-concept, a glass Fresnel lens was fabricated by precision glass
molding using a graphene-coated Si mold. For the molding setup, upper mold was a flat Si wafer while lower mold had a Fresnel lens structure, which was fabricated by a combination of ultraprecision diamond turning and RIE [10]. Again, both the upper and lower Si molds were coated with a thin graphene coating.

The Si mold is a convex Fresnel lens so the molded glass lens becomes a concave Fresnel. The molded glass Fresnel lens has a diameter of 9 mm and the nominal height of the teeth is 1 \( \mu \)m. As shown in Fig. 4(a), the microstructure of the molded glass lens was again measured using the Wyko NT9100 optical profilometer. A comparison between the lens surface and the mold surface is shown in Fig. 4(b).

The image quality of the molded glass Fresnel lens was tested by using an optical system shown in Fig. 5(a). The light source used in this experiment was a white light bulb. A light diffuser was mounted next to the light source to create a uniform illumination. A target (USAF 1951, 3" x 3" negative target, Edmunds Optics) was mounted in front of the light diffuser. Because the molded Fresnel lens is a concave lens, a standard commercial \( F/4 \) lens (double-convex lens of 25 mm diameter and 100 mm FL, Edmunds Optics) was placed behind the Fresnel lens to form a real image on the CCD. The captured image is shown in Fig. 5(b). As a comparison,

Fig. 3. (a) Surface profile of a coated Si mold. (b) SEM image of Si mold with microwells after molding. (c) Surface scan of a molded glass with micropillars. The inset is an SEM picture of the molded glass. (d) Comparison of line scans between the Si mold and the molded glass part (the profile of the Si mold was flipped for comparison).

Fig. 4. (a) Surface scan of the molded glass Fresnel lens. (b) Comparison of line scans between the molded glass lens and the Si mold (the profile of the molded glass lens was flipped for comparison).

Fig. 5. (a) Optical setup for testing the imaging quality of molded Fresnel lens. LS, light source; LD, light diffuser; \( d_1 = 690 \text{ mm}, d_2 = 86 \text{ mm}, d_3 \text{ is about } 127 \text{ mm}. \) (b) Image of the target with both Fresnel lens and commercial lens. (c) Image of the target on CCD with commercial lens alone. The molded lens was removed and CCD was placed on the focus plane of the commercial lens in this measurement.

Fig. 5(c) is the image of the target using the commercial lens alone. The two images match nicely, demonstrating the imaging quality of the molded Fresnel lens.

The durability of the carbide-bonded graphene coating was also evaluated. A graphene-coated Si wafer has been used for more than 20 times without notable signs of wearing. In the second experiment, a graphene-coated Si wafer was continuously molded at elevated temperature of 640°C for an extended time (2 h). After molding, the coating showed no signs of wearing and no changes on surface roughness were found before and after molding. These preliminary experiments have shown that the carbide-bonded graphene has the durability for high-precision glass molding applications. A quantitative study on the wear and bonding strength of the carbide-bonded graphene coating is the focus of a current research project.

It is worth noting that the carbide-bonded graphene coating technique is a low-cost process compared to other more traditional coating methods. The coating materials are inexpensive and can be obtained rather easily. High-temperature silicone rubber is a standard industrial material and is readily available. GP-SO\(_3\)H nanopaper is a newly developed material but can also be fabricated in a cost-effective way [16]. The cost of the furnace is much lower compared to other coating equipment. Moreover, thickness of the graphene coating can be controlled by adjusting the coating time and the content of coating materials, i.e., high-temperature silicone rubber and GP-SO\(_3\)H nanopaper. Current available coating thickness can be tuned from nanometers to micrometers. For the coated Si wafer used in this Letter, the thickness was about 45 nm. The thickness of coating was measured by atomic force microscopy scanning on a partially oxygen-etched graphene coating.

In conclusion, the research reported in this Letter for the first time demonstrated the use of carbide-bonded
graphene as an effective and high-performance coating material for precision glass molding. It was shown experimentally that Si-glass adhesion could be completely avoided by using the carbide-bonded graphene coating on Si molds. The coating can be applied to Si molds with or without microfeatures. As a demonstration, a glass Fresnel lens was fabricated and the molded Fresnel lens exhibits good optical performance. By using the carbide-bonded graphene coating, we expect to realize the full potential of Si as a mold material to achieve extremely low adhesion, low friction, uniform temperature distribution, and low fabrication cost for micro/nano scale precision glass optical component manufacturing.

References
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