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Rapid hot embossing of polymer microstructures using carbide-bonded graphene coating on silicon stampers

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ABSTRACT

In this study, we present a novel rapid hot micro-embossing technique utilizing micro-patterned silicon stampers coated with a newly developed carbide-bonded graphene network to implement rapid heating and cooling. The graphene coating layer is highly thermally conductive and a ~45 nm thick coating layer on silicon wafer could serve as a highly efficient heating film because of its high electrical conductivity of 1.98×10^4 S/m and low surface resistivity of 20.4 Ω. Heating rates of 5–10 °C/s could be achieved by employing a DC operating voltage under 50 V to allow the contact surface temperature of the stamper and the polymer substrate reaching glass transition temperature within 10 s for rapid embossing of microscale features. Since the graphene coating is very thin, the stamper surface could be cooled rapidly after embossing to keep the cycle time shorter than 25 s. This novel hot embossing technique was successfully implemented to imprint microchannel and microlens arrays on thermoplastic polymer substrates with high precision. Compared with conventional hot embossing, our facile method could achieve better replication fidelity with much less cycle time.

1. Introduction

With the rapid development of microscale electro-mechanical, optic-electro-mechanical and bio-electro-mechanical systems (i.e. MEMS, MOEMS and BioMEMS), cost-effective production of microstructures in large scales has gained growing attention in the industry. Polymeric materials, due to their versatile properties and mass-production capability, have considerable advantages in micro fabrication [1]. In contrast to silicon, glass, or quartz substrates, which are widely used in most MEMS, MOEMS and BioMEMS products, polymers only need a single step net-shape replication to fabricate components, instead of complicated and cleanroom based multi-step processes such as lithography.

Among various polymer micro fabrication techniques, hot embossing is a low-cost and widely used process. The popularity of this technique can be partially attributed to its simplicity in tool and process setup as compared with other competing techniques, such as micro injection molding. In addition, because of the short flow length and the quick forming of polymer, this technique is able to replicate micro-patterns on large surface areas using high molecular weight polymers [2]. In recent years, polymer devices and systems manufactured by hot embossing have demonstrated great commercial potential, especially for biomedical, telecommunication and optical applications.

However, the cycle time of hot embossing is often very long, which limits high throughput replication. An inherent problem is the large thermal mass of the embossing tool. For the standard hot embossing process, both the embossing tool and the polymer substrate need to be heated above the glass transition temperature T_g of polymer materials before embossing and then cooled to below T_g after embossing, resulting in a very slow rate of thermal cycling and consequently long cycle times in the order of 10 min or longer [3]. New techniques which can achieve rapid thermal cycling of the embossing tools are critical to overcome this drawback.

During the last decade, many researchers have attempted various techniques to achieve rapid thermal cycling in hot embossing processes. High-frequency induction heating as a variothermal process was demonstrated to be effective in productivity enhancement in both embossing [4] and micro injection molding [5,6]. Combining low thermal inertia (LTI) and embedded interconnected air channels right beneath the mold insert surface with high-frequency induction heating, the cycle time of hot micro-embossing could be reduced to ~20 s [7].

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Table 1
Comparison of properties of stamper materials used for hot embossing.

Materials	Young's modulus (GPa)	Surface hardness (GPa)	Thermal expansion coefficient (10^{-6} cm/°C)	Surface roughness Ra (nm)
Silicon (111)	160	13	2.6	0.53
Nickel (alloy 625)	193	0.8	10.6	103

Ultrasonic hot embossing of polymer micro structures is another technique to reduce the cycle time [8,9]. It could also be easily combined with ultrasonic welding to enable both imprinting and sealing of a variety of micro systems such as microfluidics devices, flow sensors, pumps, mixers, and heat exchangers. Our laboratory [10] has developed an infrared laser (laser/IR)-assisted micro embossing process to shorten the cycle time by using carbon black filled epoxy mold or polymer substrate as IR-absorbent to implement rapid and local heating. Both shorter cycle time (<10 s depending on the film thickness and the aspect ratio of the microfeatures) and good replication accuracy could be achieved. In addition, a two-station embossing process involving a hot station and a cold station to sequentially heat and cool the embossing tool for reduced cycle times in hot embossing was also developed [3]. Micro-patterned aluminum stampers could be rapidly heated from room temperature to 200 °C in 3 s using contact heating against a hot station at 250 °C and the cycle time could be reduced to ~10 s.

Although the afore-mentioned methods for rapid thermal cycling of embossing tools have achieved remarkable reduction of cycle time, complicated process modification and tool design make the hot embossing process much more expensive and less flexible as a polymer micro fabrication process. In this study, we present a facile rapid hot embossing system utilizing a novel carbide-bonded graphene coating technology on micro-patterned silicon stampers to implement rapid heating and cooling. The graphene nanosheets were cross-linked into a three-dimensional network by silicon carbide and siliconoxy carbide covalent bonds between the graphene nanosheets and between the graphene and silicon wafer surface [11]. The graphene coating layer was highly electrically and thermally conductive, where a ~45 nm thick coating layer on silicon wafer surface could reach an electrical conductivity of 1.98×10^4 S/m and an electrical resistance of 20.4 Ω. Therefore, a relatively low DC voltage could be applied on the graphene layer to achieve in-situ rapid heating. As a result, the contact surface temperature of the stamper and the polymer substrate could quickly reach $> T_g$ within seconds for rapid embossing of microstructures. Meanwhile, the whole embossing tool still remained at low temperatures and could cool down rapidly after embossing to keep the cycle time very short.

2. Experimental

2.1. Micro-feature fabrication on silicon stampers

Silicon (Si) wafers were employed to fabricate the micro-embossing stampers due to their high mechanical strength and excellent surface quality among nonmetallic materials. Both lithography based micro-patterning and high precision diamond milling machining can be easily conducted on the Si wafer surface. For most parts with microscale features, available Si wafers are large enough to serve as stampers. Table 1 compares Young's modulus, surface hardness, thermal expansion coefficient and surface roughness of silicon wafer (111) and polished nickel mold (alloy 625). Although mechanical properties are similar, Si wafer provides better surface smoothness. In this study, two Si wafers with thicknesses of 0.5 mm and 5 mm and dimensions of 15 × 15 mm and 20 × 8 mm, respectively were adapted as mold inserts to carry out the embossing experiments. For the thin Si stamper, S1813 photoresist was patterned with 2 × 2 μm lines with a 2 μm gap on Si wafer surface via standard UV photolithography. Subsequently, the exposed Si surface was etched using a combination of SF6 and He. Etching conditions (gas flow, power and time) were adjusted according to the target etch depth (i.e., ~1.5 μm). Finally, the photoresist was removed in an acetone/IPA bath to obtain the microchannel pattern. On the other hand, the thick Si stamper was machined directly on a Nanotechnology Systems' 350FG 5-axis ultraprecision machine using ultraprecision single point diamond machining. The geometry of the freeform optics feature is a 6 × 6 microlens array. Each lenslet has an overall dimension of 360 × 360 μm. The radius of curvature of each lenslet is 7.1 mm which gives the effective focal length of 12.1 mm for poly(methyl methacrylate)(PMMA) lens. For microlens array machining [12], a single point diamond tool with a relatively large radius of 3.048 mm was utilized to achieve best surface finish quality. The diamond tool was setup at a negative rake angle −24.95°. The finish cutting depth was 100 nm and the feed rate was 20 mm/min. The average surface roughness value t of the micro-milling prepared microlens array is ~15 nm (Ra) at the bottom of the concave lens surface.

2.2. Carbide bonded graphene coating of silicon stampers using CVD

The micro-patterned Si stampers were coated with a thin layer of newly developed carbide bonded graphene using chemical vapor deposition (CVD). As illustrated in Fig. 1, a liquid carbon source, benzene anhydrous (purchased from Aldrich, USA) with a purity of 99.8% in glass bubbler and a silicon source, solid PDMS, were used for graphene coating. Si wafers and PDMS were pre-placed inside a 2″ (5 cm) quartz tube of a furnace. An inert gas, argon, was applied to purge air inside the quartz tube with a flow rate of 100 SCCM for 10 min, and then the flow rate was decreased to 50 SCCM. The temperature was increased from room temperature to 950 °C (at 20 °C/min) under the inert gas

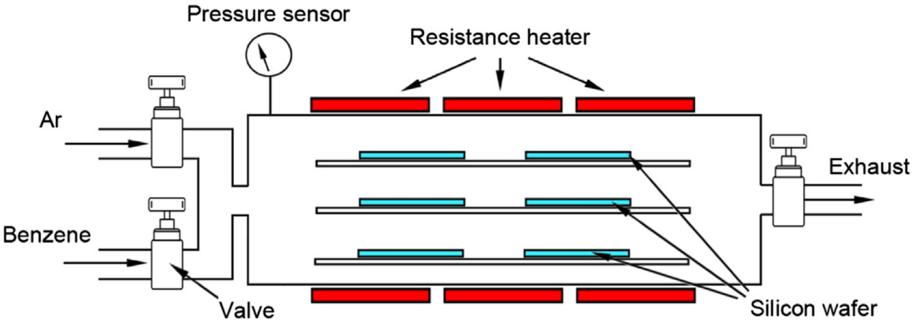

Fig. 1. Equipment for building up carbide-bonded graphene networks on Si stamper surface in a tube furnace equipped with liquid and gas lines.

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