Electrets

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Patterning of Electrostatic Charge on Electrets Using Hot Microcontact Printing**

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Dedicated to Professor George M. Whitesides on the occasion of his 70th birthday

Electrets[1] are materials that have a permanent electric field maintained either by trapping net electrostatic charge (space-charge electrets) or by holding macroscopic electric dipole moment (dipolar electrets). Dipolar electrets are fabricated by slow cooling of a dielectric material from above its glass transition temperature in the presence of a strong electric field, and space-charge electrets result from adding charge to the surface or the bulk of a material by exposing it to an electron beam or ion beam, corona charging, triboelectric charging, and so forth.[2] Besides some classic applications of electrets in electrophotography, electrostatic powder coating and electrostatic spray painting, electrostatic filters, electret microphones, and radiation dosimeters, the emerging unconventional applications of electrets reveal some startling new discoveries: by peeling pressure-sensitive adhesive tape in vacuum, Carama et al. have found an intense nanosecond X-ray pulse caused by tribocharging of insulators.[3] Liu and Bard have reported the electrostatic electrochemistry of electrets by dipping tribocharged dielectrics into solution to induce chemical reaction, such as changes in the pH value and chemiluminescence.[4] Whitesides et al. have thoroughly investigated the phenomenon of contact electrification of ionic electrets arising from the separation of ions at interfaces and have developed some powerful tools to measure the charge on tribocharged electrets before exploring their applications in electrostatic self-assembly of macroscopic crystals.[5–9]

Patterns of electrostatic charge are widely used in conventional xerography with over 100 μm resolution, and they can also serve as templates to induce the self-assembly and patterning of nanoparticles,[10,11] DNA,[12] proteins,[13] and other building blocks with sub-micrometer or even nanoscale resolution. Some serial techniques can embed charge (either electronic or ionic) into dielectric materials with patterns at resolutions smaller than 100 nm, such as electron beam lithography,[14] focused ion beam lithography,[15] and scanning probe lithography.[16] However, the expensive infrastructure required and the extremely slow writing rates of these techniques severely hinder the further applications of the nanoscale charge patterns. One parallel technique, electric microcontact printing (e-μCP),[17] employing a topographically patterned poly(dimethylsiloxane) (PDMS) stamp coated with a thin metal film, can embed charge with sub-micrometer resolution in only a few seconds. This new form of microcontact printing, which belongs to the family of soft lithography[18] techniques developed by Whitesides and co-workers, is a low-cost technique for charge printing that combines the high spatial resolution of sophisticated forms of photolithography with capabilities not present in other approaches, that is, single-step patterning of large areas (over 1 cm^2) and nonplanar surfaces. Advanced nanoxerography will enable the fabrication of a whole range of novel devices, including single-nanocomponent transistors, light-emitting diodes, lasers, sensors, passive photonic networks, or nanoparticle-based media for data storage.[19,20]

In our previous study,[21] we fabricated ultrathin metallic film along the sidewall of a PDMS stamp by incorporating nanotransfer printing (nTP)[22] techniques with edge lithography, and printed nanoscale charge patterns on PMMA film. Recently, we have used metal-coated PDMS stamps as parallel microelectrodes to selectively thermo-cross-link polymer thin films on silicon substrates[23] by applying an appropriate current between the electrodes, which induces localized heat for patterning of various materials.

Although metal-coated PDMS stamps show valuable characteristics for the patterning of electrostatic charge or soft matter, one common flaw still prevents them from broader application: electrets, precursors, polymers, self-assembly monolayers (SAMs), and other materials need to be mounted onto conductive substrates (i.e. silicon or indium tin oxide glass) as the opposite electrode to complete the patterning process. Herein, we propose a novel and simple idea for parallel patterning. By heating PDMS stamps and subsequently employing "hot" microcontact printing, a rich number of polymers and SAMs can be thermochemically patterned without needing to be supported on conductive substrates.

Figure 1 A schematically illustrates the general procedure for hot microcontact printing (μCP). A topographically patterned PDMS stamp is heated on a hot plate; immediately after being removed from the heat source, the hot stamp is conformally contacted with certain polymers or SAMs to finish the hot μCP process. PDMS is not a good thermal conductor; hence it can maintains the heat for a relatively long time to accomplish the μCP procedure. Unlike classical μCP, which uses silanes, thiols, organic or inorganic species, biomolecules, and all sorts of materials as inks, the hot μCP

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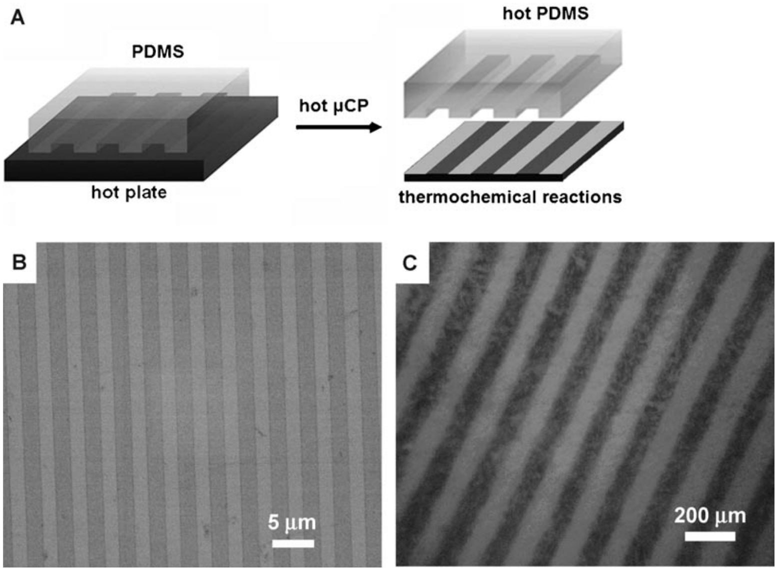

Figure 1. A) Schematic illustration, B) SEM image, and C) optical image showing the procedure and results of hot µCP of soft materials.

process prints heat energy to selectively induce chemical reactions in a very short time span.

Figure 1 B,C shows some examples of applications for hot µCP. Figure 1 B is the SEM image of a thermosensitive diazoresin film patterned by hot µCP; the PDMS stamp with 2 µm column features spaced 3 µm apart is heated above 150 °C for less than two seconds and conformally contacted with diazoresin film. The diazonium group in the diazoresin film will decompose under heating above 80 °C, while higher temperatures accelerate the reaction.[24] After being separated from the hot PDMS stamp, the diazoresin film is rinsed with aqueous NaOH to selectively remove the unreacted portions, thus generating micrometer-scale polymer structures. The optical image in Figure 1 C shows thermochromic patterns obtained after using a hot PDMS stamp to transfer heat onto chromatic ink film supported on glass. For the thermochromic ink, the area contacted with raised plateaus of the hot PDMS stamp displays an abrupt color change, while the area facing toward the trenches of the PDMS stamp shows no observable differences.

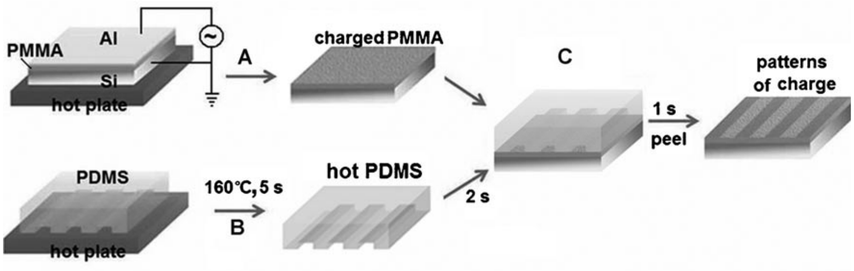

Figure 2. A schematic representation outlines the procedure of patterning electrostatic charge on electrets using hot µCP; see text for details.

Besides the thermochromic inks and thermodegradable polymer film demonstrated in Figure 1, we can easily find other chemical systems involving heat-induced changes and use this hot µCP procedure to change the material's subsequent reactivity, surface energy, solubility, conductivity, or other properties of interest. The fast, simple, and inexpensive technique shows great advantages over other thermal nanolithography methods, such as scanning probe microscopy (SPM)[25] and dip-pen nanolithography (DPN)[26] for parallel patterning of small features in large areas; moreover, the method can be used for charge patterning on bulk electrets (Figure 2), which is difficult or even impossible to accomplish using alternative means.

There are many different ways to generate or embed charge into electrets: orientation of permanent dipoles (in polar materials); trapping of charge by structural defects and impurity centers; buildup of charge near heterogeneities or the grain boundaries in polycrystalline materials; and contact electrification, isothermal charging, and penetrating radiation.[1] Generally, it is quite difficult to investigate the various mechanisms of charge storage and charge decay in electrets at room temperature, because at such low temperatures the dipoles and space charges remain virtually immobile. An effective method, thermally stimulated discharge (TSD),[1] was developed in the early 20th century to characterize the intrinsic properties of electrets by heating the dielectrics to accelerate discharging. With the TSD technique, the dipoles and space charges quickly regain their freedom of motion when electrets are heated to restore electrostatic charge neutrality.

The schematic illustration in Figure 2 shows the procedure for patterning electrostatic charge on electrets using hot µCP, a process resembling a TSD technique that selectively discharges electrets under heat. Step A in Figure 2 is a typical thermal charging process: A thin layer (100 nm) of poly(methylmethacrylate) (PMMA) film supported on a silicon wafer is uniformly charged at 150 °C under an electric field of 10 kV cm^{-1} by using aluminum foil as electrode to apply electric potential. After being charged for 10 min, the PMMA film and electrodes are removed from the hot plate while the electric field is still applied until the system cools down to room temperature. After this step, electrostatic charges are uniformly stored in PMMA electrets. Step B in Figure 2 shows the procedure of heating a topographically patterned PDMS stamp. After being in contact with a hot plate at 160 °C for five seconds, a 1 mm thick stamp can be uniformly heated; after being removed from the hot plate, the hot PDMS stamp is treated by a stream of nitrogen to cool down the air inside the bottom trench. Step C in Figure 2 illustrates the hot µCP procedure: uniformly charged PMMA electrets are conformally contacted with the hot PDMS stamp for a short time and then quickly removed; the topographically patterned PDMS stamp transfers and prints "heat" selectively onto PMMA film; the heat neutralizes the space charges or releases the dipole charges from electrets during a thermally stimulated discharging (TSD) process. The area facing toward the bottom trench of the PDMS stamp remains charged. Patterns of electrostatic charge on electrets can be produced, because the large difference in the coefficient of heat transmission between air and PDMS enables the temperature to be kept relatively low during the short contact time, which makes it possible not to induce discharge from the noncontacted area.

It is worthy to note that in step A in Figure 2, the electrets need not be supported on a conductive Si substrate to be charged by an electric field, because many other charging methods could be applied. Herein we choose PMMA films supported on Si wafer as electrets in order to characterize the charge patterns by Kelvin probe force microscopy (KFM), a tool to measure electrostatic potential through an electric cycle. The atomic force microscopy (AFM) image in Figure 3A shows the surface topography of the PMMA film during the hot μCP process, and the flat surface morphology indicates that there are no observable differences in topography before and after the hot μCP operation. The KFM images in Figure 3B–D show a set of surface potential changes after hot μCP. From these images, we can clearly see that the technique can generate various electrostatic charge patterns on PMMA thin-film electrets with different geometries and length scales, which are determined by the features of the PDMS stamp. Figure 3E,F shows the morphology and surface potential images of a thin film (with thickness around 200 nm) of poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP), a polymer with a typical ferroelectric charging and discharging mechanism. Strong electric field can orient and "freeze" its dipole group (e.g. the CF_2 moiety) within crystalline domains at room temperature, while hot μCP can selectively release the dipole moment through a thermally stimulated depolarization (TSD) process.[27,28] Figure 3G,H shows the topography and corresponding surface potential images of a 2 μm feature PDMS stamp; the AFM image shows clear-cut vertical edges for the features in the stamp, while the KFM image shows similar geometry and length scale with fuzzy edges, which are mainly caused by the thermal diffusion and hierarchical discharge during hot μCP.

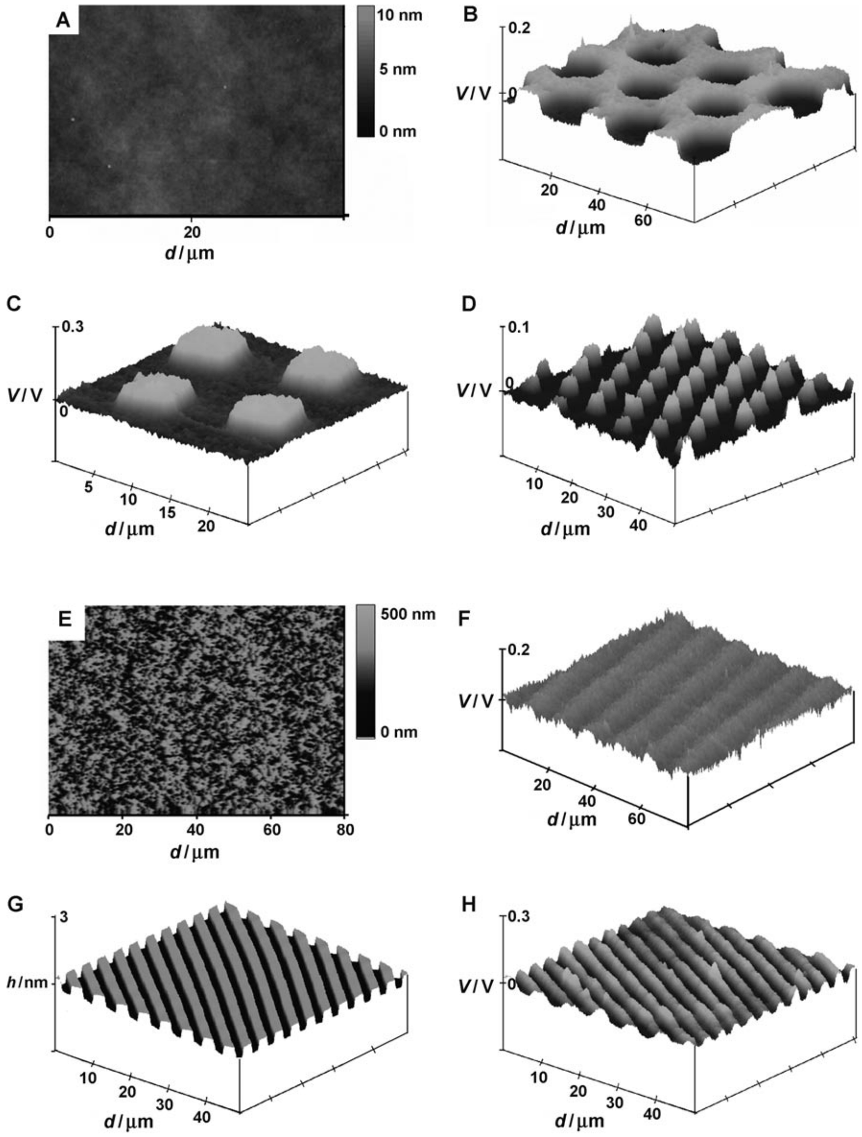

Figure 3. A) AFM and B–D) KFM images obtained from hot μCP show the topography and surface potential differences on PMMA thin film. E) AFM and F) KFM images show the hot μCP procedure on PVDF-HFP thin film. G) AFM shows the topography of a 2 μm feature PDMS stamp and corresponding charge patterning image (H) using the stamp, as shown by KFM.

Charge patterns on electrets can attract micro- and nanoparticles, a phenomenon that is widely applied in photocopiers and nanoxerography. Figure 4 shows a set of SEM and optical images that display the patterns of nanoparticles and microbeads adsorbed on electrets. The SEM images in Figure 4A,B show the adsorption of silica nanoparticles with 500 nm diameters from their ethanol suspension; the optical images in Figure 4C,D show the adsorption of platinum and Fe_2O_3 nanopowder of from dry state. The charge patterns on PMMA electrets can be stable in air for over one month,[17] and the nanoparticle microstructures can stay much longer than that without further treatment.

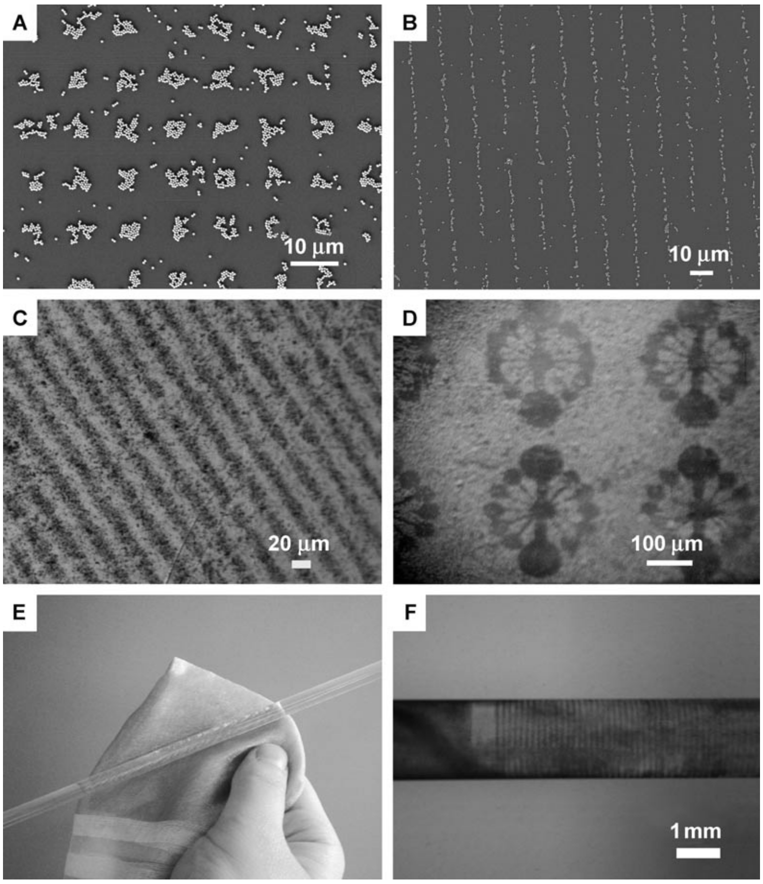

Figure 4. Adsorption of microbeads and nanoparticles on charge patterns generated by hot µCP. A, B) 500 nm silica microbeads adsorbed on charge patterns on PMMA thin film. C, D) Pt nanopowder and nanosized Fe_2O_3 particles adsorbed on an organic glass (bulk PMMA) with charge patterns. E) Optical photograph of a classical tribocharging process. F) Carbon toner adsorbed on glass rod with charge patterns.

The adsorption of nanoparticles is an excellent application for charge patterns on electrets; furthermore, it can be treated as a powerful method to characterize microscale and nanoscale charge patterns in bulk electrets as a substitution for KFM, which is unable to obtain an electric response through thick dielectric layers. The photograph in Figure 4E illustrates a classic contact electrification process:[29] a glass rod is rubbed with a silk cloth to generate space charges. A hot, topographically patterned PDMS stamp rolls over the charged glass rod, and heat from the features of the PDMS stamp is transferred to print the glass rod for thermal discharging. After these processes, carbon toner particles are evenly spread onto the glass rod and developed into microscale line patterns (Figure 4F) by blowing away the loosely held material in a stream of dry nitrogen. Since tribocharging using a silk cloth can inevitably roughen the surface of materials, we have not generated sub-micrometer and nanoscale charge patterns and subsequently nanoparticle patterns on the bulk electrets. However, it is reasonable to imagine that hot µCP is capable of patterning electrostatic charge at the nanometer scale on the smooth surface of bulk electrets if an alternative charging method such as electron beam irradiation is used.

In conclusion, we demonstrate herein a very simple and inexpensive procedure to transfer and print “heat” to induce chemical reactions and charge dissipation on solid surfaces. The versatile method, hot microcontact printing (hot µCP), using heat energy rather than materials as ink, should be a useful supplement to soft lithography and can greatly expand the range of soft-matter patterning. The ability to pattern electrostatic charges on bulk and thin-film dielectrics makes the technique a unique tool in exploring new applications of electrets, as high-resolution charge patterns are extremely useful in data storage, nanocomponent optoelectronics, and self-assembly systems.

Experimental Section

All materials and chemicals were purchased commercially and used as received. Poly(vinylidene fluoride-*co*-hexafluoropropylene), poly(methylmethacrylate), platinum nanopowder, and Fe_2O_3 nanoparticles were purchased from Aldrich. Thermochromic inks (composed of transition-metal complexes) were purchased from Beijing Chenlei Technology Development Co. Other chemical reagents were purchased from Sinopharm Chemical Reagent Beijing Co. All the AFM images were recorded using a Veeco D3100 instrument and the SEM images were recorded with a JEOL 7401 microscope. Optical images were recorded with a Nikon TE2000-U optical microscope.

Fabrication of PDMS stamps: Soft lithography and rapid prototyping were used to fabricate features in SU-8 (Micro-chem Corp.) that were subsequently replica-molded using PDMS prepolymer to fabricate the flexible stamps.

Thermal chemical patterning of diazonium resin: Diphenylamine diazonium salt and diazoresin (DR) were synthesized according to literature procedures.[30] DR was dissolved in water to form a 1 $mg\,mL^{-1}$ solution and dip-coated onto a clean silicon wafer. The wafer with thermosensitive polymer was contacted with a hot PDMS stamp and then developed by a 0.01 M NaOH solution to generate DR microstructures.

Patterning of charge on PMMA film supported on Si substrate: PMMA was dissolved in chlorobenzene to form a 2% solution and spin-coated at 6000 rpm to form a thin film on a doped, electrically conductive Si wafer. The film was heated at 180 °C for 0.5 hour in a vacuum oven. The PMMA thin film was contacted with a piece of aluminum foil, which served as another electrode. A Keithley 2400 electrometer was used as power supply to apply direct current through the film on a 150 °C hot plate to accomplish thermocharging. The voltage was kept at 10 $kV\,cm^{-1}$ (the current through PMMA thin film is around 2 mA) until the temperature of the hot plate decreased to 25 °C. After thermal charging, the PMMA film was removed from the power source and conformally contacted with hot, topographically patterned PDMS to accomplish hot µCP or thermal discharging.

Adsorption of nanoparticles and microbeads on charge patterns: The charged PMMA film was immersed into a 0.5% w/v suspension of silica particles or polystyrene microspheres (500 nm) in ethanol for 60 seconds and quickly rinsed with ethanol to wash away particles loosely held on uncharged areas.

The PMMA plates (organic glass) and glass rod were rubbed with silk cloth for a few seconds and contacted with a topographically patterned PDMS stamp (previously heated at 160 °C). The tribocharged organic glass and glass rod were immersed into dry powders of micro- or nanoparticles of carbon toner, Pt, or Fe_2O_3; the patterns were developed by blowing away the loosely held particles in a stream of dry nitrogen.

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