

preferred. In the double-layer structure the two carrier types are separated and the recombination zone is located at the internal interface. Thus, to build up LED devices from PBD and TH a separated double-layer structure is preferable. The EL intensity observed at 530 nm is weak. However, it may be increased by using another electrode material for electron injection. Absolute regulation of the luminance will be solved in the future. The results imply that new LEDs can be built up from polymers with TH and PBD monomer units.

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## Elastomeric Light Valves\*\*

By Dong Qin, Younan Xia, and George M. Whitesides\*

This paper describes the fabrication and performance of two new types of light valves. In the first type, an elastomeric block of poly(dimethylsiloxane) (PDMS) having approximately square pyramidal features on its surface was prepared by molding against a Si(100) master whose surface was etched into a regular array of square pits; the faces of these pits met in dihedral angles of  $54^\circ$ , and they efficiently reflected light propagating through the polymer and into the patterned surface. In the second type, an elastomeric block having an array of corner cubes on its surface was fabricated by replica molding against a commercial reflective tape. PDMS is an isotropic elastomer that is optically transparent down to  $\sim 300$  nm.<sup>[1]</sup> Using PDMS as our starting material, we are exploring new optical components and devices whose characteristics can be controlled by changing their shape by means of mechanical compression or extension. We have demonstrated the concepts of elastomeric optics whose surface can be changed by mechanical

strain with several examples—lenses,<sup>[2]</sup> mirrors,<sup>[2]</sup> diffraction gratings,<sup>[2,3]</sup> photothermal detectors,<sup>[4]</sup> and optical modulators.<sup>[5]</sup> The deformable elastomeric light valves fabricated here could have applications in display devices,<sup>[6]</sup> energy-saving windows,<sup>[7,8]</sup> sensors (accelerometers and pressure gauges),<sup>[9]</sup> and photolithographic systems (as photomasks).<sup>[10]</sup>

Figure 1 outlines the procedure used to generate the first type of light valve. A silicon master having an array of square pyramidal cavities on its surface was fabricated using a published procedure—a combination of microcontact printing ( $\mu$ CP) of hexadecanethiol on silver, selective removal of underderivatized silver in an aqueous ferricyanide solution, and anisotropic etching of Si(100) in an aqueous solution of KOH/2-propanol.<sup>[11,12]</sup> A liquid prepolymer of PDMS was poured over the Si master, cured to a solid material, and removed by peeling it away from the master. This PDMS block was then sandwiched between two glass plates; the air-gap between the PDMS block and one of the glass plates was filled with an opaque dye solution (crystal violet in tri(ethylene glycol)) by capillary filling.<sup>[13,14]</sup> The

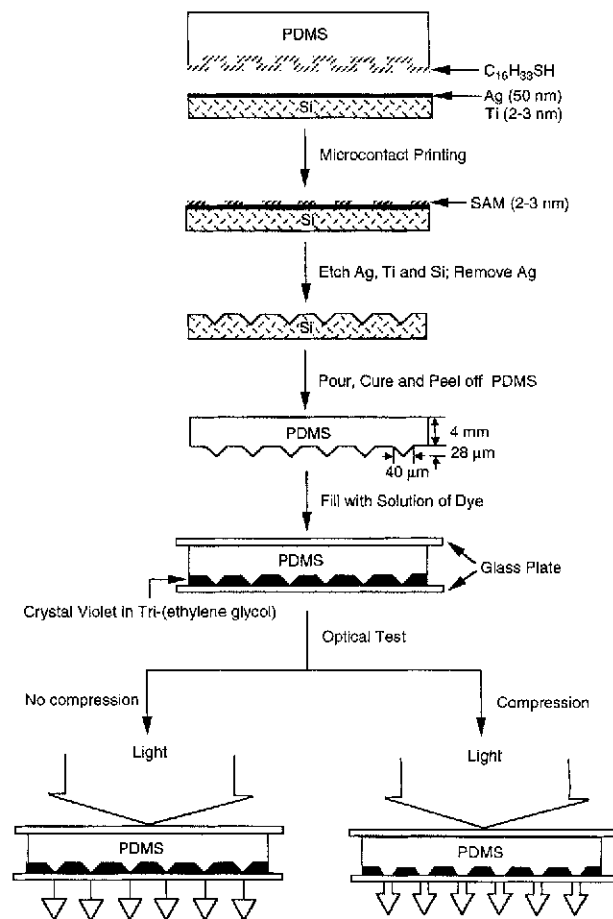


Fig. 1. Schematic procedure for fabricating the first type of elastomeric light valve. We changed the size of the apertures, and therefore the ratio of transmitted to absorbed light, by applying vertical pressure against the two glass plates. The compressive strain on the PDMS block controlled the amount of light transmitted through the light valve.

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size of the aperture—that is, the area of the patterned surface of the PDMS in contact with the surface of one of the two glass plates—could be changed by compression. The vertical pressure applied to the two glass plates changed the ratio of transmitted to absorbed light. Without compression, light passed only through the tips of the pyramidal features on the PDMS; it is completely blocked by the dye solution over the rest of the area of the PDMS surface. When pressure was applied vertically against the glass plates, the tips of the pyramidal features were deformed; as a result, the size of the apertures and the intensity of the transmitted light increased.

Figure 2A shows an SEM image of the silicon master having an array of pyramidal cavities on its surface. Figure 2B shows an optical micrograph (in transmission mode) of the first type of light valve. The PDMS block was

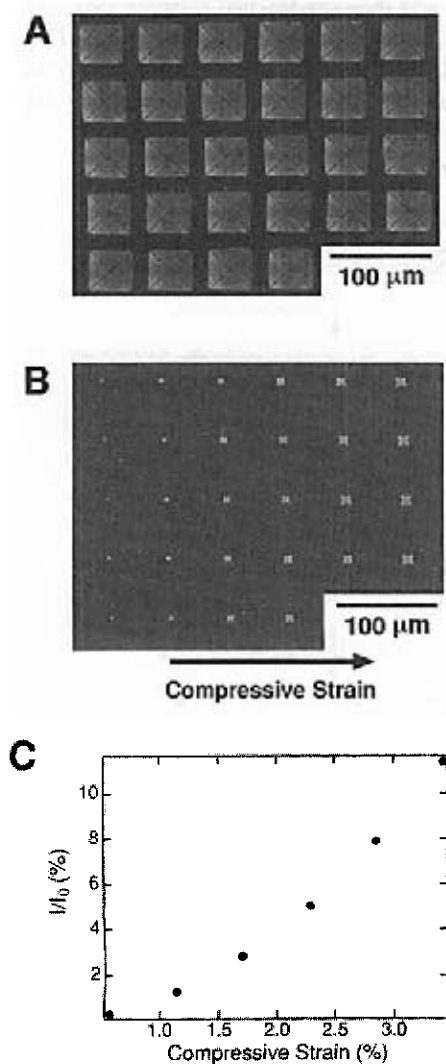


Fig. 2. A) An SEM image of the etched Si(100) that was used to make PDMS replicas. B) An optical micrograph (in transmission mode) of an array of light valves under an asymmetrical compression (the compressive strain increased from left to right). C) The dependence of the intensity of transmitted light (normalized to the incident intensity of the light) on the compressive strain.

compressed unevenly across the surface: the pressure increased continuously from left to right. Figure 2C shows the relationship of the intensity of transmitted light to the compressive strain. Since the opaque dye layer is a liquid, this type of light valve is reversible: the dye solution squeezed out during compression returns on release.

The second type of light valve was fabricated by casting against an array of corner cubes presented on a retroreflective tape using a three-stage procedure (Fig. 3). First, an epoxy replica was prepared by casting against the relief surface of a retroreflective tape (Jogslite, Silver Lake, NH). Second, this epoxy replica was used as the master to prepare PDMS replicas. Third, a PDMS block was sandwiched between two glass plates for optical measurements. The three reflecting faces of a corner cube are arranged at right angles to each other.<sup>[14]</sup> Therefore, light that enters from the front surface is reflected back out of the front surface due to total reflection (Fig. 3D). The light transmitted through this PDMS light valve could, therefore, be manipulated by deforming the PDMS corners through vertical pressure applied against the glass plates: the deformed regions of the corner become transparent since total reflection no longer occurs.

Figure 4A and B show SEM images of the retroreflective tape (with corner-cube-shaped microstructures on its surface) and the PDMS replica, respectively. Figure 4C shows the measured intensity of transmitted light (He-Ne laser,  $\lambda = 632 \text{ nm}$ ) as a function of compressive strain. This type of light valve is also reversible. The measurements indicated that the intensity of the transmitted light changed by  $\sim 25 \text{ dB}$  over a range of compressive strain from 0 to  $\sim 20\%$ . In order to confirm the proposed mechanism of operation

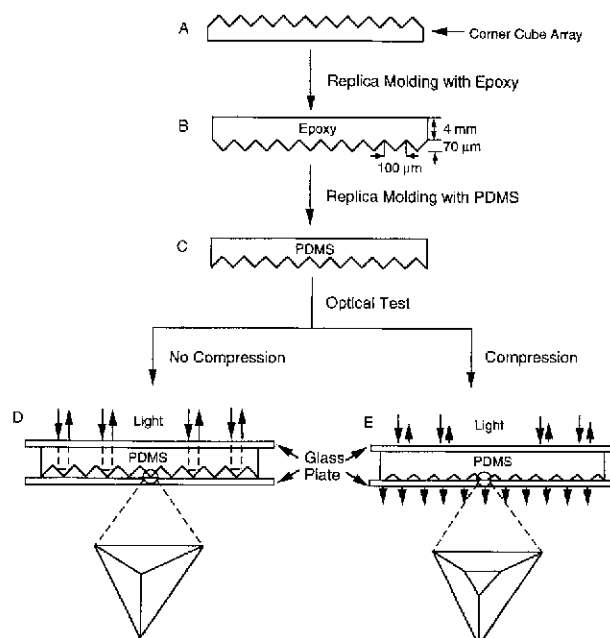


Fig. 3. Schematic outline of the procedure for fabricating an elastomeric light valve using an array of corner cubes.

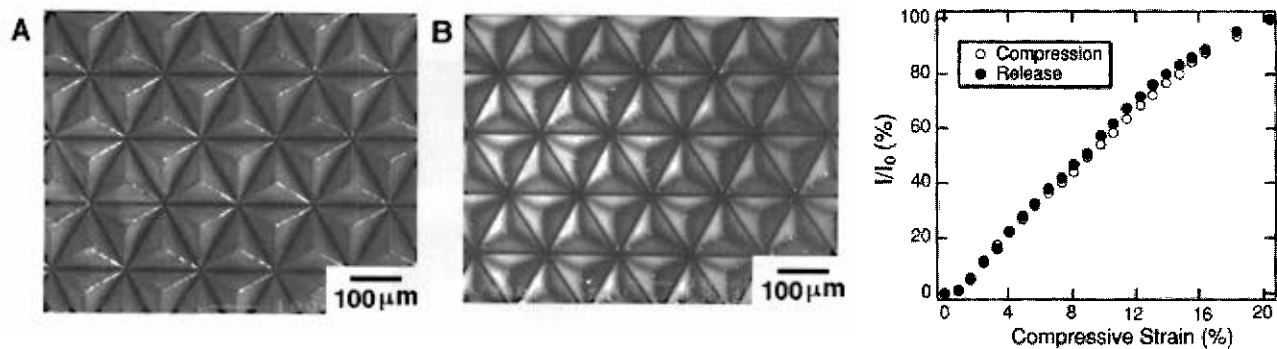


Fig. 4. SEM images of the reflective tape (A) and the PDMS replica (B). C) The dependence of the intensity of the transmitted light (normalized to the incident intensity of light) as a function of the compressive strain on PDMS. The intensity of the transmitted light from this array of light valves changed by  $\sim 25$  dB over a compressive strain of  $\sim 20\%$ .

of this type of light valve, we made replicas of the PDMS structure under different compressive strains by molding with epoxy (Fig. 5). The tips of the corner cubes became quasi two-dimensional structures as the compression increased; an array of these compressed structures was transparent to the incident light. The pressure applied against the two glass plates changed the ratio of transmitted to reflected light. The higher the compressive strain on this light valve, the more light was transmitted through it.

These deformable light valves could be used as components of display devices.<sup>[6,16]</sup> Figure 6 demonstrates two examples of such devices based on the type of light valve illustrated in Figure 3 (that is, a device based on retroreflective elements). Figure 6A shows an optical micrograph of

the pattern used in these experiments. Figure 6B shows the optical micrograph of this pattern when this light valve was placed on top of it. As we discussed above, before compressing, this light valve was "off"; the pattern was invisible. When we applied mechanical pressure to the two glass plates, the valve turned "on" and the pattern became visible (Fig. 6C). We could also turn on the light valve (Fig. 6D) by filling the air gap between one of the two glass plates and the patterned surface of the PDMS block with a liquid (in this case ethanol). The liquid changed the parameters that had produced total internal reflection; the light valve became transparent to the incident light. The resolution of these devices is  $\sim 100$   $\mu\text{m}$ , a value that is limited by the feature size of the corner cubes. With the availability of

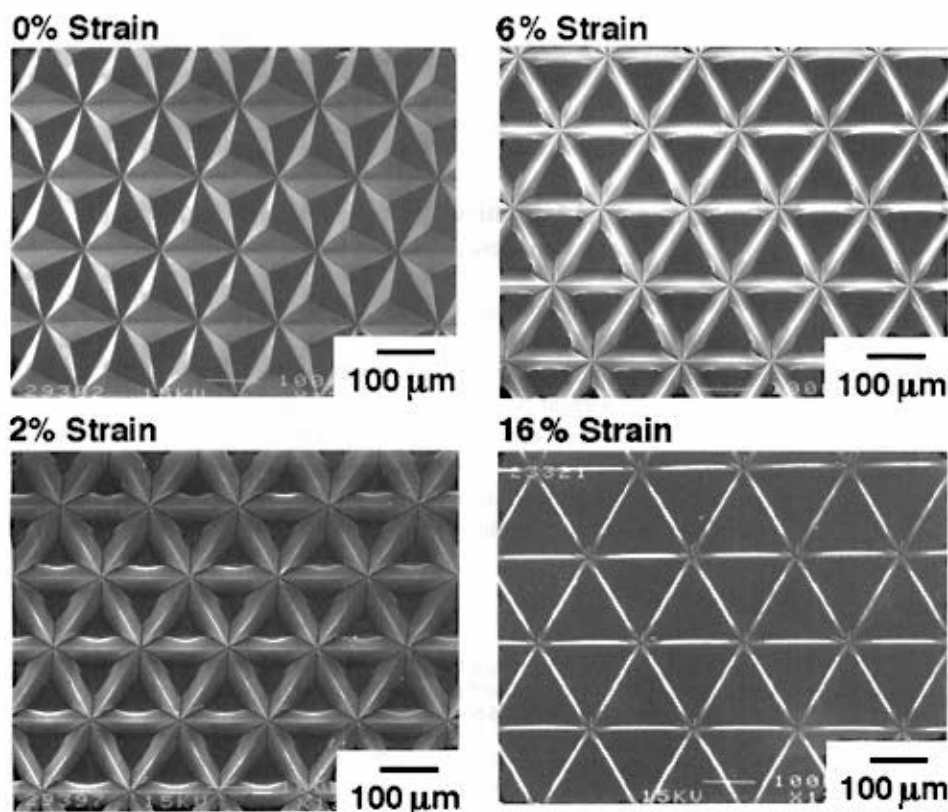


Fig. 5. SEM images of epoxy replicas cast from a PDMS mold (Fig. 4B) under different compressive strains. These images establish that the corner cubes gradually changed from a three-dimensional corner-cube structure into a quasi two-dimensional structure as compressive strain increased.

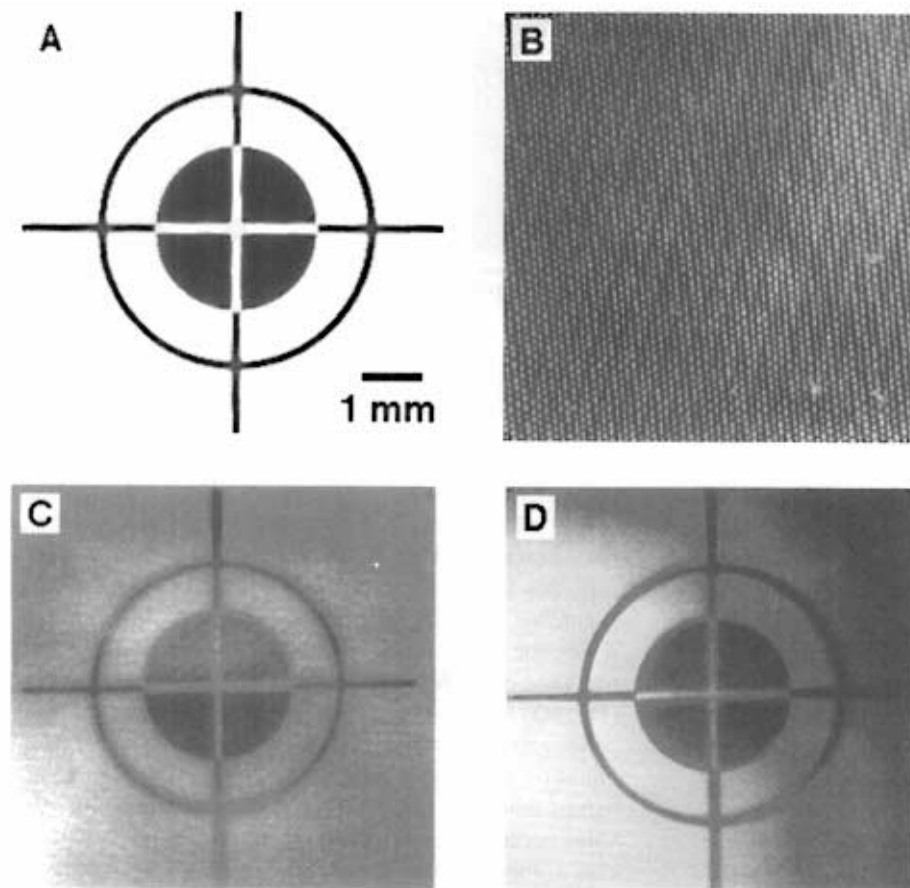


Fig. 6. Optical micrographs to show the application of the second type of light valve in a display (see the text for details).

smaller corner cubes, we believe we should be able to fabricate display devices with a theoretical pixel size of less than  $100 \mu\text{m}^2$ .<sup>[17]</sup>

In summary, we have fabricated two types of elastomeric light valves by replicating PDMS elastomer against an anisotropically etched Si(100) or an array of corner cubes. The elastomeric character of PDMS allows us to control the amount of light transmitted through these light valves by mechanical compression.

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### 3D Organized Self-Assembled Monolayer Electrodes: A Novel Biosensor Configuration\*\*

By Srinivasan Sampath and Ovidia Lev\*

Organized self-assembled nanostructures have attracted a great deal of interest in recent years.<sup>[1-3]</sup> Enhanced electrical communication between biomolecules and gold electrodes was demonstrated<sup>[4-6]</sup> and remarkable limits of detection of dissolved analytes were attained.<sup>[7,8]</sup> However, all these applications utilize planar electrode surfaces,

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