Nanometer scale patterning and pattern transfer on amorphous Si, crystalline Si, and SiO_2 surfaces using self-assembled monolayers

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Microcontact printing was used to form nanometer scale patterns of self-assembled monolayers (SAMs) on amorphous Si, crystalline Si, and SiO_2 using octadecyltrichlorosilane (OTS) as the ink and an elastomer as the stamp. The patterns were subsequently transferred into crystalline Si substrates or amorphous Si films using the SAM of OTS as the resist film. Atomic force microscopy was used to characterize the quality of the SAM and the resulting patterns. Using a Si pillar structure as the master, "pancakes" of less than 80 nm in size were formed by over etching of the patterned OTS film on amorphous Si using KOH. The size of the resulting amorphous Si pancakes can be controlled by the etching time. © *1997 American Institute of Physics.* [S0003-6951(97)02912-4]

Techniques such as *e*-beam lithography,[1] x-ray lithography,[2] scanning probe microscopy based lithography[3–5] and others, have been used to fabricate structures with sizes <100 nm. Although it is possible to generate these feature sizes, the manufacturability of these techniques in a high throughput microelectronics fabrication environment is still a concern.

Microcontact printing is a technique that can generate patterns of self-assembled monolayers (SAMs) of alkanethiolates on surfaces of gold,[6] silver,[7] and copper,[8] or of alkysiloxanes on hydroxyl-terminated surfaces.[9,10] The patterned SAM can serve as a thin resist film with which the patterns can be transferred to a substrate utilizing an appropriate etching method. Much of the work in this area has been performed on gold. An aqueous solution of ferricynide is used as a wet etchant to transfer the SAM patterns to the thin gold film, which can then serve as a secondary mask to etch underlying semiconductor layers.[7,11] Improved processes are needed before microcontact printing can be considered as a serious candidate for a semiconductor manufacturing process.

In this letter, we report on the formation of patterned SAM films on SiO_2, crystalline Si, and amorphous Si surfaces. The patterns were transferred successfully to the amorphous Si and crystalline Si surfaces using only the SAM as the resist film and KOH as the etchant. Amorphous Si films resulted in the smallest pancakes (about 80 nm in diameter). The dimensions of the SAM films and the etched patterns were verified by atomic force microscopy (AFM).

Figure 1 illustrates the procedure of microcontact printing and subsequent pattern transfer used in our experiments. Two kinds of master wafers were used to make the polydimethylsiloxane (PDMS) stamps. The first master is a film of photoresist patterned by photolithography; and the size of the structures is on the order of microns. The second master is composed of Si dots and lines formed by *e*-beam lithography. The dimension of the structures is on the nanometer scale. AFM images of the Si nanostructures are shown in Figs. 2(a) and 2(b). The pitch of the dots in Fig. 2(a) is 250 nm, and the diameter of the dots is approximately 150 nm. The pitch and width of the lines are 500 and 300 nm, respectively from the figure. However, due to the AFM tip shape, the actual size of the dots and the line width should be 50, 100 nm, respectively. The stamps, which can be used repeatedly, were then cast from these masters.

The substrates used for microcontact imprinting were amorphous Si, crystalline Si, and SiO_2. The formation of the amorphous silicon film (20 nm) was achieved by room temperature *e*-beam evaporation of silicon onto a SiO_2 substrate. The surface roughness of all the substrates prior to processing was better than a few nanometers. Before contacting with the stamp, the surface was treated in a solution of 30% H_2O_2 and concentrated H_2SO_4 to yield a thin SiO_2 film with a Si–OH group concentration of about 5×10^{14} cm^{-2};[12,13] thus, the surface is highly hydrophilic. A dilute octadecyl-

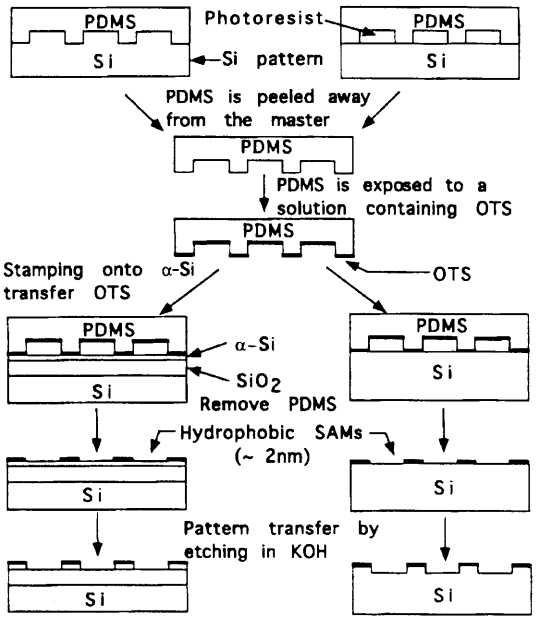

FIG. 1. Schematic of the procedure for microcontact printing.

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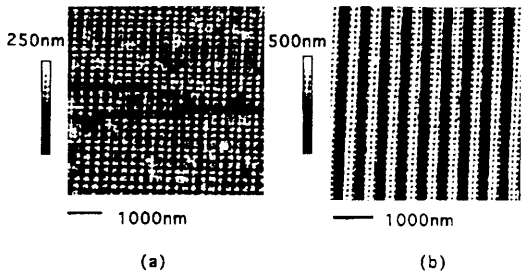

FIG. 2. AFM images of a master formed by *e*-beam lithography, showing the Si array of (a) nanometer scale dots and (b) lines. The pitch of the dots is 250 nm and the XXXXX is about 150 nm. The pitch of the lines is 500 nm and the linewidth is about 300 nm. The height of the dots and lines is about 350 nm.

trichlorosilane (OTS) solution (one drop in 10 ml hexane) was prepared in a N_2 atmosphere using hexane as the solvent since OTS reacts violently with water. A cotton swab was used to apply the OTS onto the surface of the stamp. The stamp was then brought into contact with the substrate. The Si–Cl bonds in the OTS molecules are broken by the OH groups present on the surface of the substrate to form a network of Si–O–Si bonds, resulting in a self-assembled monolayer of OTS on the contact area. Longer contacting time and stronger applied force result in a more resilient OTS layer, which can better withstand the subsequent processing. In this experiment, the substrate and stamp are kept in contact for more than a few minutes (in this case, we let the stamp in contact for more than 2 h).

Figures 3(a) and 3(b) are typical AFM images of the nanometer scale SAM patterns formed on the amorphous Si surface. The height and width of the SAM lines shown in Fig. 3(b) is approximately 2 and 100 nm, respectively.

Pattern transfer was successful for OTS on both amorphous and crystalline Si by the use of a dilute KOH etching solution. In this process, the wafer is dipped in dilute HF for about 8 s to remove the native oxide prior to KOH etching. Figures 4(a) and 4(b) are AFM images of the transferred line patterns on crystalline Si and amorphous Si, depicting a rougher surface for the case of OTS on the crystalline Si surface. The surface roughening is caused by the anisotropic etching of crystalline Si by KOH. This problem is circumvented by the use of an amorphous silicon film. As can be seen in Fig. 4(b), after the pattern transfer, the amorphous Si

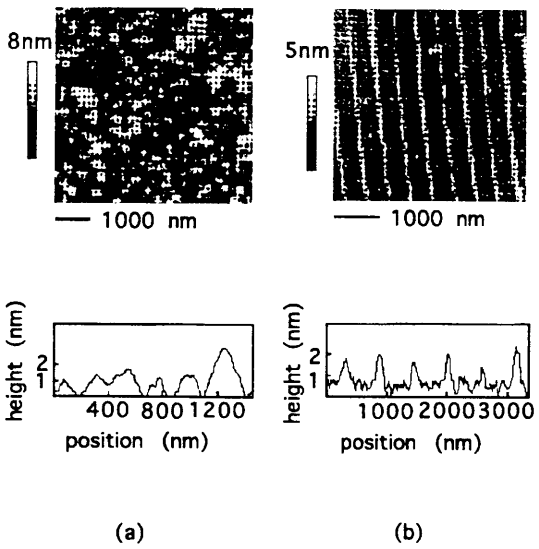

FIG. 3. AFM images of nanometer scale SAM patterns formed on the amorphous Si surface by microcontact printing. Their thickness is about 2 nm. (a) and (b) are the AFM images of the SAMs formed by the master wafers shown in Figs. 2(a) and 2(b), respectively.

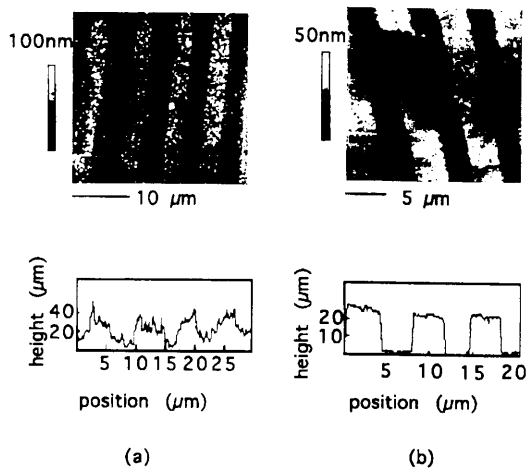

FIG. 4. AFM images of line patterns formed on (a) crystalline Si and (b) amorphous Si after dilute KOH etching with the OTS monolayer as masks. The etch depth is about 20 nm and the linewidth is on the order of microns.

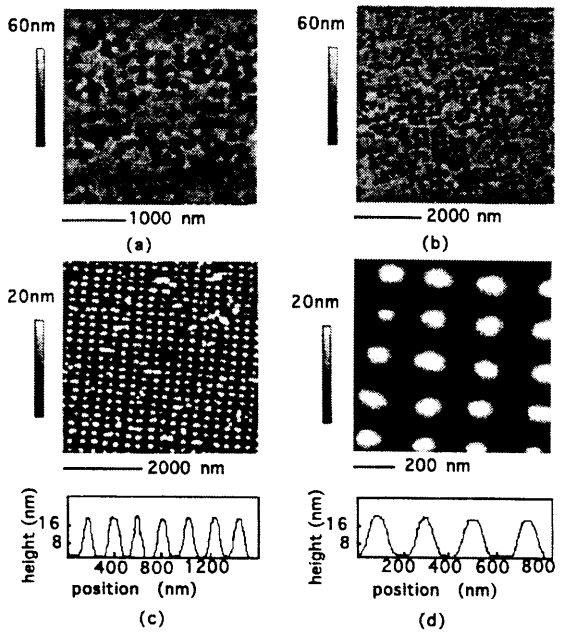

FIG. 5. AFM images of the transferred patterns on the amorphous Si surface after etching by dilute KOH: (a) and (b) showing the images of the hole patterns. Their pitch is 250 nm, the same as that of the master wafer. The images of the amorphous pancakes, with the diameter of 80 nm, are illustrated in (c) and (d). These pancakes are obtained after over etching with KOH.

surface of the patterns is smoother relative to that in the crystalline Si case. The use of amorphous Si as a transfer layer constitutes a substantive improvement over the metal films more commonly used in microcontact printing, since amorphous silicon is compatible with current Si technology.

As illustrated in Fig. 1, the patterns formed by wet etching of SAMs are the inverse of the original patterns of the master wafer. Since the master wafer, shown in Fig. 2(a), has a pillar pattern, the pattern transferred onto the substrates will be holes, with a diameter equal to the base of the pillars. Figures 5(a) and 5(b) are the AFM images of the holes formed on the amorphous Si surface after etching by dilute KOH. Their pitch is 250 nm, the same as that on the master wafer. When the hole pattern is overetched during pattern transfer to the extent that holes touch each other, a pancake pattern results. The size of the pancakes can be controlled by the etching time. Figures 5(c) and 5(d) show the amorphous pancakes with a diameter of 80 nm. This amorphous Si pancake pattern can be used as a secondary mask for subsequent patterning if desired. In the case of pattern transfer on a SiO_2 film, we found that the OTS film is not able to withstand etching by HF. Therefore, we have been unable to successfully transfer a pattern to a SiO_2 film. Alternative methods for pattern transfer must be used.[10]

In summary, we have demonstrated the use of microcontact printing to form nanometer scale SAM patterns on amorphous Si, crystalline Si, and SiO_2 surfaces. Pattern transfer was successful only on a crystalline Si substrate and an amorphous Si film. AFM images show that the patterns on the amorphous Si film have a smoother surface. Amorphous Si pancakes of 80 nm in diameter were formed by this method. Smaller patterns can be made from masters with smaller feature sizes.

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