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Fabrication of Highly-Ordered Nanopatterned Copper Nanowire Arrays by Photolithography

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Two different patterns, one being circular and the other being QDU, of copper (Cu) nanowire arrays were successfully produced by electrochemical deposition and photolithography. The highly-ordered patterns of Cu nanowire arrays were observed to stand freely on the substrate using scanning electron microscopy (SEM). Chemical analyses have been performed on Cu nanowires using energy dispersive X-ray spectroscopy (EDS). The results confirmed that it is mainly composed of Cu. Selected-area electron diffraction (SAED) pattern indicated the nanowires are single crystalline and the growth direction of the nanowires is along the [220] direction. With the deposition time increasing, the length of Cu nanowires increaseed.

Keywords: Pattern, Photolithographic Method, Nanowire Arrays, Electrodeposition.

1. INTRODUCTION

Recent innovation in the micro- and nanofabrication has created a unique opportunity for patterning surfaces with features spanning from nano- to milli-meter range in lateral dimensions. Micro- and nanometer-scale patterns can be obtained by photolithography,[1–4] electron beam lithography,[5,6] soft lithography,[7] micro-contact printing(μCP).[8–11] These techniques have partially the same process: they can transfer patterns onto surface of a substrate. With the development of nanotechnology, a variety of industries, such as biosensor,[12] proteomic arrays[13] and multifunctional coatings,[14] have focused on obtaining patterns with the smallest possible lateral dimensions.[15] Among above mentioned techniques, *photolithography is one of the most successful techniques in large-scale microfabrication.*[16] The method is effective, low-cost and simple implementation. Researchers have successfully patterned gold nanowires on the surface AAM *via* photolithography.[1] Here we use this method to make two different Cu nanowire patterns. Due to their electric conduction and potentially useful applications, large-area Cu nanowire patterns will be used in microdevices.

Many methods have been developed for the fabrication of nanowires. Template synthesis is considered to be very useful because it can be used to prepare different types of nanostructures. Much previous work has focused on the fabrication of copper nanowires,[17,18] since they show high electrical conductivity and are suitable for potential applications such as electronic devices.[19] In this paper, we report an effective procedure for the fabrication of patterned nanowire arrays with micrometer-scale features. This process starts with the fabrication of patterned AAO templates. Then the Cu nanowires are selectively deposited into the modified templates. Finally, the morphology and microstructure of nanowire arrays have been investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). This method is suitable for patterning various nanomaterials, such as metal nanowires, semiconductor and polymer nanostructures. The one-dimensional nano-arrays can be applied in many fields. Especially, metal nanowire arrays will be used in microdevices and integrate circuits because of their magnetism and conductivity. In this paper, we mainly master this fabrication method, and then will apply these patterned Cu nanowire arrays in gas ionization sensors and introduce other performances.

2. EXPERIMENTAL DETAILS

2.1. Materials

Porous AAO template (Whatman Anodisc 25) with an average pore diameter of 200 nm (actually from 200 to 300 nm) was treated in alcohol in an ultrasonic bath to

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clean its surface. The photoresist is the type of BP-212. The photo-mask is a special piece of glass with patterns on one side, and blank on the other side. When the ultraviolet light goes through the patterns, they will be transferred onto the substrate.

2.2. Preparation of Patterned AAO Membrane

The membrane was spin-coated with a layer of photoresist at 2700 rpm for 30 sec to seal the pores of the AAO template, then "soft baked" at a low temperature in order to remove the solvents from the photoresist and to improve photoresist-AAO template adhesion. Afterwards, the composite was covered with a photolithographic mask and exposed to ultraviolet (wavelength $\lambda = 365$ nm), and "hard baked" at a higher temperature to further activate the cross-linking process and to improve the mechanical stability of the pattern,[20] and was subsequently developed in a developer, flushed with deionized distilled water several times and dried in nitrogen. The pores of AAO were selectively opened only in the exposed areas.

2.3. Electrodeposition of Cu Nanowires

The patterned side of the membrane was sputtered with a layer of Au as a work electrode. In a tri-electrode system, the Cu nanowires were selectively deposited into the open pores using an electrolyte solution of 0.5 mol/L $CuSO_4$ + 0.1 mol/L H_2SO_4. The electrodeposition was carried out using platinum as an anode and a calomel electrode as a reference electrode. Finally, the patterned nanowire arrays were revealed by removal of AAO in a 3 mol/L sodium hydroxide solution. The schematic diagram of the fabrication process of Cu nanowire arrays is shown in Figure 1.

2.4. Characterization of Cu Nanowires

The morphology of the patterns was investigated using a JEOL JSM-6390LV SEM. The structure and microstructure of the Cu nanowires are investigated using a JEOL JEM-2000EX TEM. The specimen for TEM observation was prepared by evaporating a drop (5 μL) of the nanowire dispersion onto a carbon-film-coated copper grid.

3. RESULTS AND DISCUSSION

Figure 2 shows SEM images of patterned AAO templates and Cu nanowire arrays with circular patterns. Figure 2(a) presents a typical SEM image of patterned AAO template formed by photolithography. The patterns were completely transferred onto the surface of AAO templates. The distance between two adjacent patterns is 5 μm just like that in the masks. As shown in Figure 2(b), the pores were selectively opened in pattern, and were sealed by the photoresist around the pattern. From Figure 2(c), we can tell

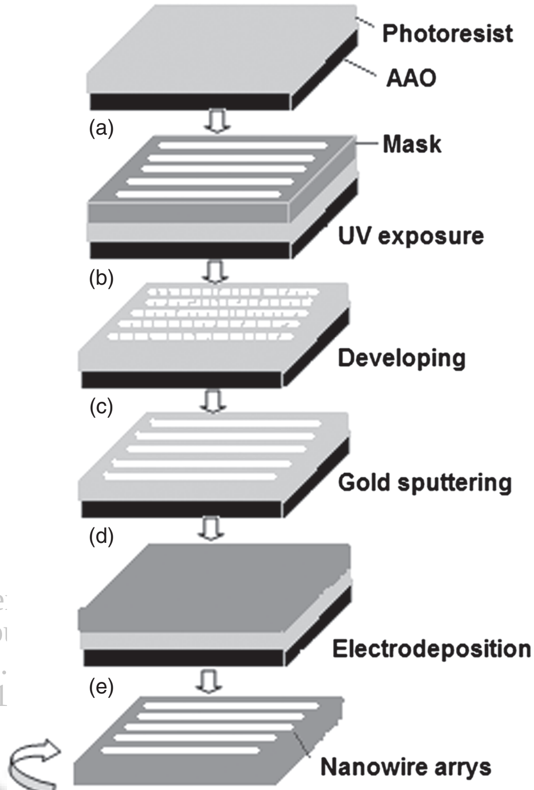

Fig. 1. A schematic diagram of the fabrication process: (a) Coating of photoresist onto the AAO, and the composites covered by mask; (b) Exposure of the composites to UV; (c) Selective opening of the AAO pores by dissolving the exposed area in a developer; (d) Sputtering of a gold layer on the patterned side of the membrane; (e) Formation of patterned nanowire arrays by electrochemical deposition, the arrow shows that the Cu nanowires were deposited onto the Au film through the AAO, and then the composite was turned over.

that the distance between two adjacent patterns is 5 μm and the nanowire patterns have a diameter of 5 μm. An enlarged SEM image in Figure 2(d) reveals that the length of the free-standing nanowires is 3–4 μm. It is believed that when template was dissolved away, the nanowires inclined to agglutinate together to minimize free energy of the system.[21]

We can fabricate not only circular patterns, but also various patterns by changing the dimensions of the masks used in photolithographic process. Highly-ordered large area QDU patterns were obtained using the same method, and the SEM images of QDU pattern are shown in Figure 3. From Figure 3(a), it can be clearly seen that the whole rows and lines are regular in arrangement, and the distance between two adjacent lines and rows is about 50 μm, respectively. An enlarged SEM image of the QDU pattern is shown in Figure 3(b). From Figure 3(b), we can clearly see that the QDU patterns are well ordered, and the distance between the three letters is equal, about 4 μm, and the width and length of each letter is 50 μm and 70 μm, respectively. The patterns are the same as those of AAO template. Figure 3(c) shows well-proportioned diameter of

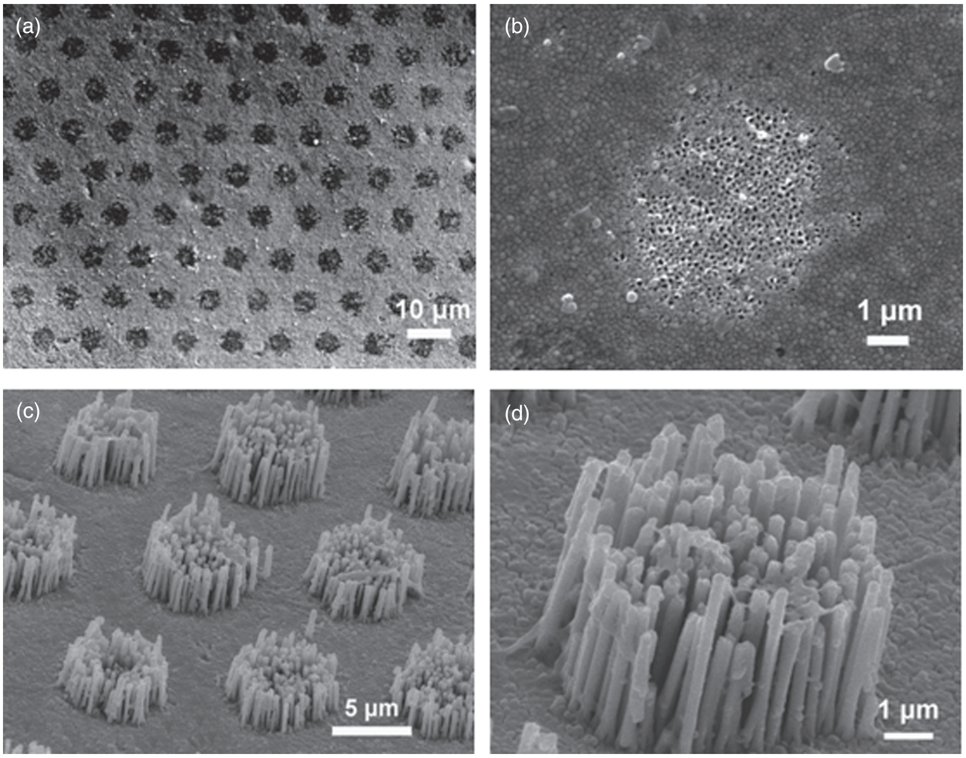

Fig. 2. SEM images of patterned AAO templates and Cu nanowire arrays: (a) Patterned AAO template with circular patterns; (b) An enlarged pattern in Figure 1(a); (c) SEM image of Cu nanowire arrays showing a circular pattern; (d) An enlarged SEM image of the pattern in figure (a).

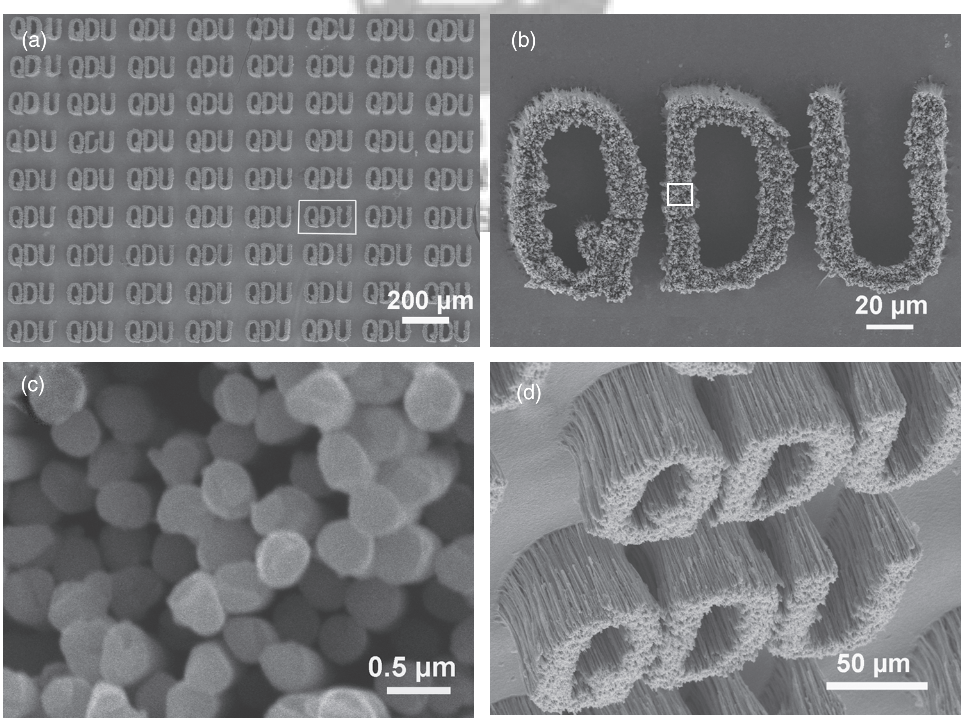

Fig. 3. Typical SEM images of Cu nanowire arrays with QDU patterns: (a) Large area QDU patterns; (b) A magnified image of the structure boxed in figure (a); (c) A higher-magnification SEM image of the structure boxed in figure (b); (d) The side image shows the length of the Cu nanowires in figure (b).

Table I. Experimental conditions for the different samples.

Sample	Electrolyte	Electrodeposition time (min)	Electrodeposition voltage (V)
Sample 1	0.5 mol/L $CuSO_4$ + 0.1 mol/L H_2SO_4	5	−0.6
Sample 2	0.5 mol/L $CuSO_4$ + 0.1 mol/L H_2SO_4	20	−0.2

the nanowires. The pattern was tilted to reveal the length of the vertical nanowires using SEM, and the SEM image is shown in Figure 3(d). From Figure 3(d), the length is measured to be approximately 50 μm (the depth of AAO is 60 μm), and the line width of the letters is about 15 μm.

Compared with Figure 2(b), it can be seen that the nanowires are longer and more ordered in Figure 3(c). The length and orderliness of the nanowires depend on the experimental conditions. The experimental conditions for the preparation of these samples are summarized in Table I. Sample 1 has a circular pattern (Fig. 2), while sample 2 has a QDU pattern (Fig. 3). On one hand, as shown in these two SEM images, the nanowires differ in length. This is due to the different electrodeposition time. The length of the wire is 3–4 μm for 5 min and about 50 μm for 20 min in deposition, respectively. Under the same experimental conditions, the relationship between length and time is shown in Figure 4. From Figure 4, it can be seen that the length of the nanowires increases with the electrodeposition time.

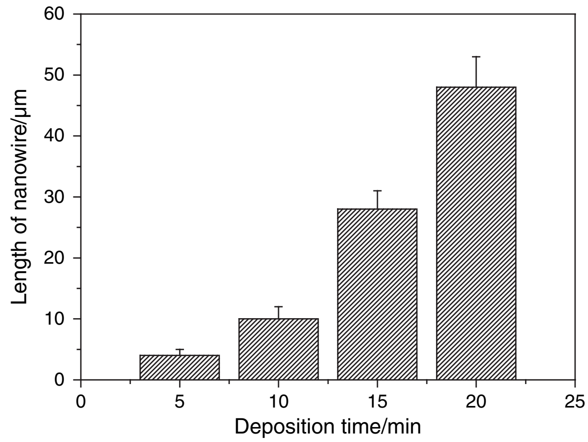

Fig. 4. The relationship between deposition time and length of wires.

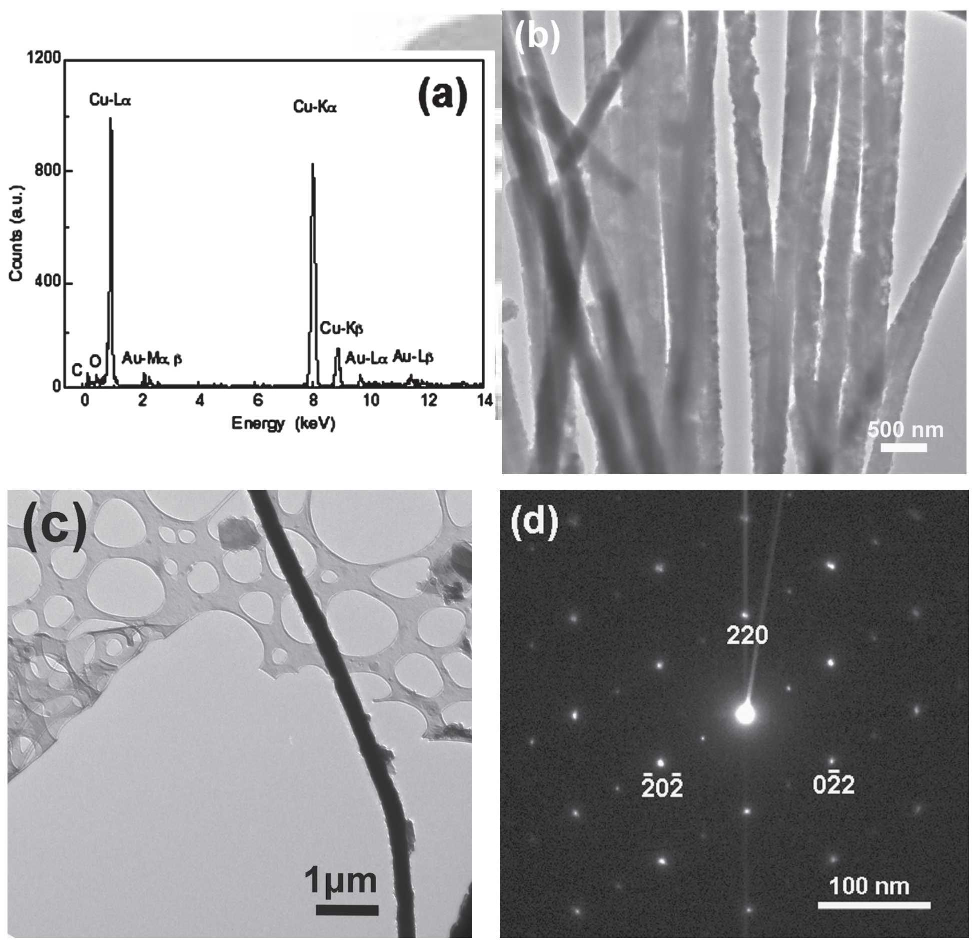

Fig. 5. (a) EDS spectrum of Cu nanowires in Figure 3(c); (b)–(d) TEM investigation of the individual Cu nanowire: (b) Bright-field image of the Cu nanowire array; (c) A single Cu nanowire; (d) The corresponding SAED pattern taken from the nanowire shown in figure (c).

On the other hand, the rate of deposition can affect the uniformity of the nanowires. Due to the difference in the thickness of the barrier layer at each pore, the deposition rate becomes different at each pore. Compared Figure 2(d) with 3(d), low speed (−0.2 V) makes the wires more uniform in length than those obtained at high speed (−0.6 V).

The chemical composition of the nanowires was investigated using the energy dispersive X-ray spectroscopy (EDS). The EDS spectrum in Figure 5(a) shows that it is mainly composed of Cu with very small amount of gold, carbon and oxygen. The small amount of carbon comes from the photoresist. Usually, the photoresist does not be removed, but can be removed in sodium hydroxide solution when AAO is removed. So some photoresist may be residual. The small amount of oxygen may come from copper oxide the can not be removed completely, and the oxidation of copper takes place readily in the air.

The structure and microstructure of an individual Cu nanowire were characterized by TEM after the AAO template had been thoroughly dissolved. TEM images in Figure 5(b) shows that the Cu nanowires were dense, continuous and uniform in diameter throughout the entire length of the wires. The diameter distribution of the wires was obtained using the statistical results of more than 50 nanowires. The results show that the diameters of the Cu nanowires are from 200 nm to 300 nm, in good agreement with those of the channels in the AAO template. Figure 5(c) presents that a single nanowire bent when applied external force, but not break. The result indicates the Cu nanowires have good mechanical properties.

Figure 5(d) shows the corresponding selected area electron diffraction (SAED) pattern, respectively. The SAED pattern of the Cu nanowire does not change along the length of the wire. This indicates that the nanowire is single crystalline. From the SAED pattern, we can tell that the growth direction of the nanowires is along the [220] direction, which is consistent with the report from other groups.[22]

4. CONCLUSION

We have successfully fabricated two different large-area patterns of copper nanowire arrays through combining photolithography and electrochemical deposition at room temperature. The highly-ordered patterns have uniform structures and stand freely on the substrate after removal of AAO template. The length of the nanowires can be controlled by the electrodeposition time, and the uniformity by deposition rate. Meanwhile, the growth direction of nanowires was examined from the SAED pattern. Based on the EDS and TEM images, the composition and structure of the Cu nanowires are confirmed. The approach described here can be applicable to fabricate a variety of nanowire patterns in different diameters. Our group is working progressively in this field,[23] and is trying to assemble microdevices using metal nanowire arrays with patterns obtained by the photolithography.

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References and Notes

1. F. Li, M. Zhu, C. G. Liu, W. L. Zhou, and J. B. Wiley, *J. Am. Chem. Soc.* 128, 13342 (**2006**).
2. B. D. Gates, Q. B. Xu, M. Stewart, D. Ryan, C. G. Willson, and G. M. Whitesides, *Chem. Rev.* 105, 1171 (**2005**).
3. J. C. Love, D. B. Wolfe, H. O. Jacobs, and G. M. Whitesides, *Langmuir* 17, 6005 (**2001**).
4. Z. Babak, *Langmuir* 21, 20 (**2004**).
5. H. Elsner and H. G. Meyer, *Microelectron. Eng.* 291, 57 (**2001**).
6. K. Yamazaki and H. Namatsu, *Microelectron. Eng.* 85, 73 (**2004**).
7. M. Denoual, L. Griscom, H. Toshiyoshi, and H. Fujita, *Jpn. J. Appl. Phys. Part* 1 42, 4598 (**2003**).
8. L. B. Goetting, T. Deng, and G. M. Whitesides, *Langmuir* 15, 1182 (**1999**).
9. H. Schmid and B. Michel, *Macromolecules* 33, 3042 (**2000**).
10. P. M. St. John and H. G. Craighead, *Appl, Phys. Lett.* 68, 1022 (**1996**).
11. E. S. Györvary, *Nano Lett.* 3, 315 (**2003**).
12. K. Kuwabara, M. Ogino, and S. Motowaki, *A. Miyauchi Microelectron. Eng.* 752, 73 (**2004**).
13. K. L. Christman, M. V. Requa, V. D. Enriquez-Rios, S. C. Ward, K. A. Bradley, K. L. Turner, and H. D. Maynard, *Langmuir* 22, 7444 (**2006**).
14. H. Lee, S. M. Dellatore, W. M. Miller, and P. B. Messersmith, *Science* 318, 426 (**2007**).
15. G. M. Wallraff and W. D. Hinsberg, *Chem. Rev.* 99, 1801 (**1999**).
16. E. S. Györvary, A. O'Riordan, A. J. Quinn, G. Redmond, D. Pum, and U. B. Sleytr, *Nano Lett.* 3, 315 (**2003**).
17. R. Inguanta, S. Piazza, and C. Sunseri, *Electrochem. Commun.* 10, 506 (**2008**).
18. T. Gao, G. W. Meng, J. Zhang, Y. W. Wang, C. H. Liang, J. C. Fan, and L. D. Zhang, *Appl. Phys. A* 73, 251 (**2001**).
19. S. V. Kalinin, D. A. Bonnell, T. Alvarez, X. J. Lei, Z. H. Hu, R. Shao, and J. H. Ferris, *Adv. Mater.* 16, 795 (**2004**).
20. A. Del Campo and E. Arzt, *Chem. Rev.* 108, 911 (**2008**).
21. C. L. Xu, H. Li, T. Xue, and H. L. Li, *Scripta Mater.* 54, 1605 (**2006**).
22. M. E. Tomil Molares, J. Brötz, V. Buschmann, D. Dobrev, R. Neumann, R. Scholz, I. U. Schuchert, C. Trautmann, and J. Vetter, *Nucl. Instrum. Methods Phys. Res. Sect. B* 185, 192 (**2001**).
23. X. R. Li, G. J. Song, Z. Peng, X. L. She, J. J. Li, J. Sun, D. Zhou, P. D. Li, and Z. J. Shao, *Nanoscale Res. Lett.* 3, 521 (**2008**).

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