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14. ABSTRACT Nanowires of various materials and configurations have been shown to be highly effective in the detection of chemical and biological species. In this paper, we report a novel nanosphere-enabled approach to fabricating highly sensitive gas sensors based on ordered arrays of vertically aligned silicon nanowires topped with a periodically porous top electrode. The vertical array configuration helps to greatly increase the sensitivity of the sensor while the pores in the top electrode layer significantly improve sensing response times by allowing analyte gases to pass through freely. Herein, we show highly sensitive detection to both nitrogen dioxide (NO2) and ammonia (NH3) in humidified air. NO2 detection down to 10 parts per billion (ppb) is demonstrated and an order-of-magnitude improvement in sensor response time is shown in the detection of NH3.					
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Periodically porous top electrodes on vertical nanowire arrays for highly sensitive gas detection

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Abstract

Nanowires of various materials and configurations have been shown to be highly effective in the detection of chemical and biological species. In this paper, we report a novel, nanosphere-enabled approach to fabricating highly sensitive gas sensors based on ordered arrays of vertically aligned silicon nanowires topped with a periodically porous top electrode. The vertical array configuration helps to greatly increase the sensitivity of the sensor while the pores in the top electrode layer significantly improve sensing response times by allowing analyte gases to pass through freely. Herein, we show highly sensitive detection to both nitrogen dioxide (NO₂) and ammonia (NH₃) in humidified air. NO₂ detection down to 10 parts per billion (ppb) is demonstrated and an order-of-magnitude improvement in sensor response time is shown in the detection of NH₃.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Highly sensitive detectors for chemical and biological species are critically important in both commercial and military applications. To this end, much effort has been expended on developing direct electrical readout ChemFET-type sensors that incorporate semiconducting nanowires [1–4]. Nanowires are used mainly because their small size and huge surface-to-volume ratios render their electrical conductivities uniquely sensitive to surface analyte adsorption [5]. However, to date, the commercialisation of such devices has been very limited due to several significant problems. These include slow serial processing of individual devices, unreliable results due to irreproducible nanowire dimensions and surface chemistry, size-dependent noise sources such as $1/f$ noise and substrate electrical effects such as trapping–detrapping of charge carriers and adsorbates.

Chem/biosensors consisting of large parallel arrays of nanowires mitigate some of these problems and exhibit particularly high sensitivity due to the increased surface area of multiple nanowires as well as reduced noise levels that result from the averaging out of charge-carrier-dependent noise

sources [6, 7]. While several methods for creating such nanowire array sensors have been demonstrated [4, 6–9], achieving controllability over nanowires and their junctions in a fast, repeatable and scalable fabrication process remains challenging. The performance of nanowire sensors can be further enhanced by using vertically aligned nanowires. This configuration maximises the surface area of the nanowires in contact with the environment while minimising the deleterious effects of the substrate on nanowire sensing [10]. Additionally, the ultra-dense placement of nanowires maximises the sensing area per device, which can be further increased without incurring an additional footprint by using longer nanowires. For these reasons, a vertical array of highly regular and periodically placed nanowires is a configuration well suited for sensing applications.

The main challenge in creating a chem/biosensor based on large arrays of vertical nanowires lies in making an electrical connection to the top of each nanowire in the array. The substrate itself typically serves as the bottom electrode, but a top electrode that reliably connects to all the nanowire tips in the array is more difficult to fabricate. An existing approach involves embedding the entire nanowire array in a sacrificial

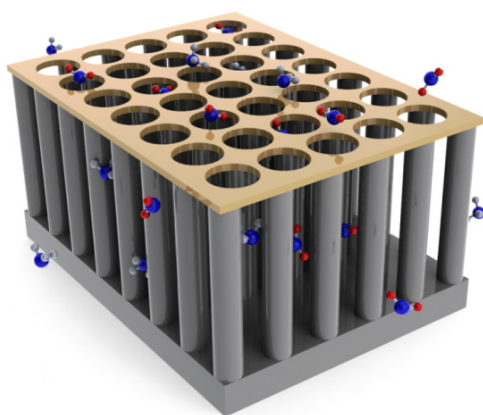


Figure 1. Schematic illustration of the periodically porous top electrode (PTE) nanowire array sensor concept.

material, exposing the tips of the nanowires, and depositing the top contact electrode [3, 11, 12]. With this approach, the nanowire sensing region is exposed upon removal of the sacrificial material. However, because the top electrode layer is non-porous, analyte gases can only enter from the periphery of the nanowire array and must subsequently traverse a labyrinthine network of nanowires. This delays the response and unequally exposes the nanowires at the edge and centre of the array. Attempts to overcome this problem include the deposition of a porous gold nanoparticle film on top of the nanowire array [13] and the random gap-bridging of nanowires during growth [14]. These methods improve the sensing response by allowing the analyte to directly reach the nanowires, but the size and distribution of analyte pathways cannot be precisely controlled. More importantly, the resulting nanowire-to-electrode or nanowire-to-nanowire connections are inherently random and inconsistent. Porous electrodes may also be formed by using electron beam (e-beam) lithography [15] or focused-ion-beam (FIB) milling [16],

but the serial and time-intensive nature of such processes preclude them from being used in large-area or large-batch applications.

We demonstrate a quick, repeatable and scalable new method for creating chem/biosensors based on large arrays of vertically aligned nanowires. Our approach uses two separate nanosphere lithography steps to first create large, well-ordered arrays of vertical nanowires and then fabricate a periodically porous top electrode that makes consistent electrical connections to every nanowire in the array (figure 1). A periodically porous top electrode, henceforth referred to as PTE, is an electrode layer lying on top of the nanowire array that is packed with uniform holes of controllable size and distribution. Fast and highly sensitive detection of ammonia and nitrogen dioxide in humidified air using the PTE nanowire array sensor configuration is demonstrated.

2. Methods and materials

In this study, a combination of nanosphere lithography and metal-assisted chemical etching was used to first synthesise well-ordered arrays of silicon nanowires (SiNWs) [12]. Silicon was chosen for its ease of fabrication and integration as well as the wide availability of various functionalisation and surface modification techniques for increased sensitivity and selectivity [1, 4, 17–20]. Precise control over dopant type and concentration is available in commercially obtained wafers. Our process started with a 100 mm diameter B-doped p-type Si(100) wafer of resistivity $\sim 10 \Omega \text{ cm}$ that was cut into 1 cm^2 pieces and successively cleaned in a 3:1 solution of $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2(30\%)$, 1:1:5 solution of $\text{H}_2\text{O}_2(30\%):\text{NH}_4\text{OH}:\text{H}_2\text{O}$ and deionised water. The resulting hydrophilic substrate was then spin-coated [21] (figures 2(a) and 3(a)) with a close-packed monolayer of 490 nm polystyrene nanospheres (Bangs Laboratories, 10% w/v). The nanospheres were subsequently reduced in diameter via an

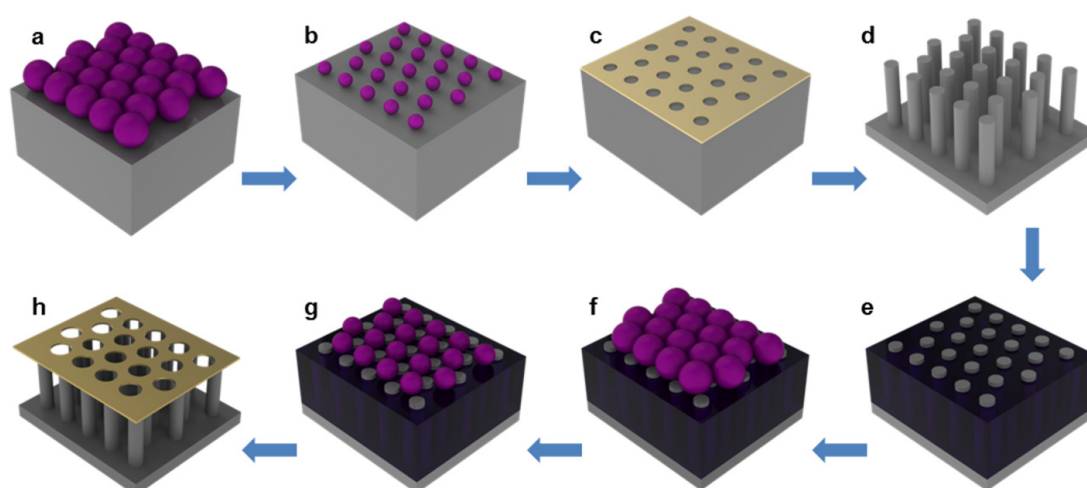


Figure 2. Outline of the nanowire sensor fabrication process: (a) spin-coat monolayer of close-packed nanospheres; (b) reduce nanosphere diameter in oxygen plasma; (c) deposit catalyst material for Si etching and rinse away nanospheres; (d) catalytic, anisotropic etching of Si; (e) embed nanowire array in thick photoresist and etch back in oxygen plasma to reveal nanowire tips; (f) spin-coat second monolayer of close-packed nanospheres; (g) reduce nanosphere diameter in oxygen plasma; and (h) deposit top electrode material and dissolve away nanosphere and photoresist layers.

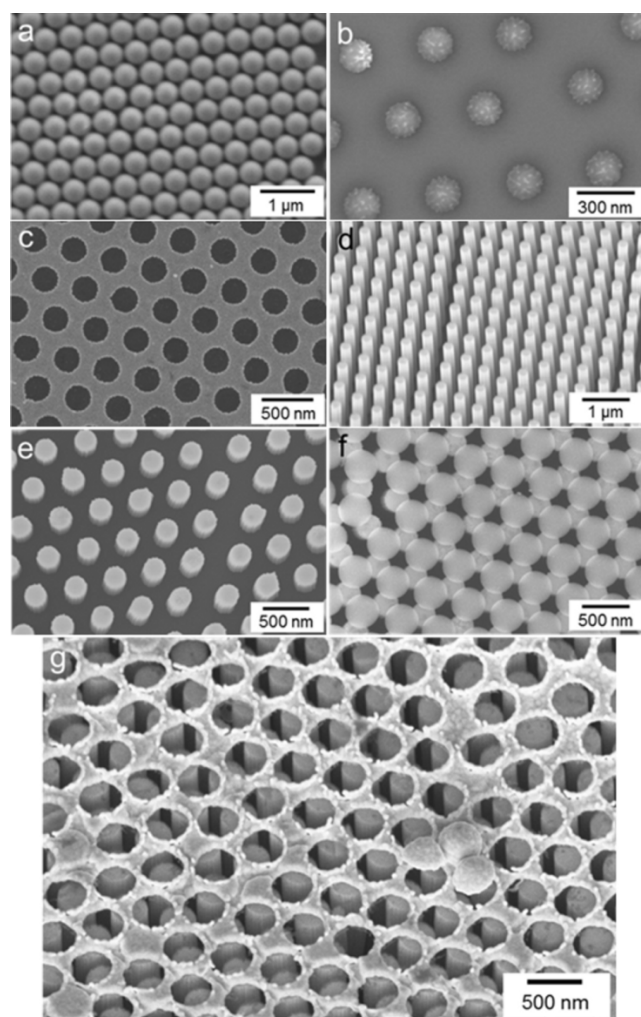


Figure 3. Scanning electron microscope (SEM) images of the sensor at various stages in the fabrication process: (a) close-packed monolayer of polystyrene nanospheres; (b) nanospheres with oxygen-plasma-reduced diameters; (c) Au etch template for Si etching; (d) vertical SiNW array; (e) exposed tips of the SiNW array embedded in photoresist; (f) second layer of nanospheres perfectly occupying gaps in the SiNW array; and (g) completed device showing the PTE and the SiNW array underneath.

oxygen plasma etch (figures 2(b) and 3(b)). A perforated gold template for the catalytic anisotropic etching of silicon was created by evaporating a 25 nm thick layer of gold on top of the nanosphere array and subsequently removing the nanospheres by soaking in CHCl_3 (figures 2(c) and 3(c)). The SiNWs were then formed by immersing the device in a solution of 10% HF and 0.6% H_2O_2 , where gold selectively and anisotropically etched into the silicon substrate, leaving behind a well-ordered array of vertically standing nanowires (figures 2(d) and 3(d)). A photoresist layer could be patterned over parts of the template to prevent the etching of silicon in certain locations, such as the contact pad region (figure 4(a)). The silicon etch rate in the HF– H_2O_2 solution depends on multiple factors, including solution concentration, temperature, template dimensions, etc, but was shown to be approximately 200 nm min^{-1} in our case. Our samples were

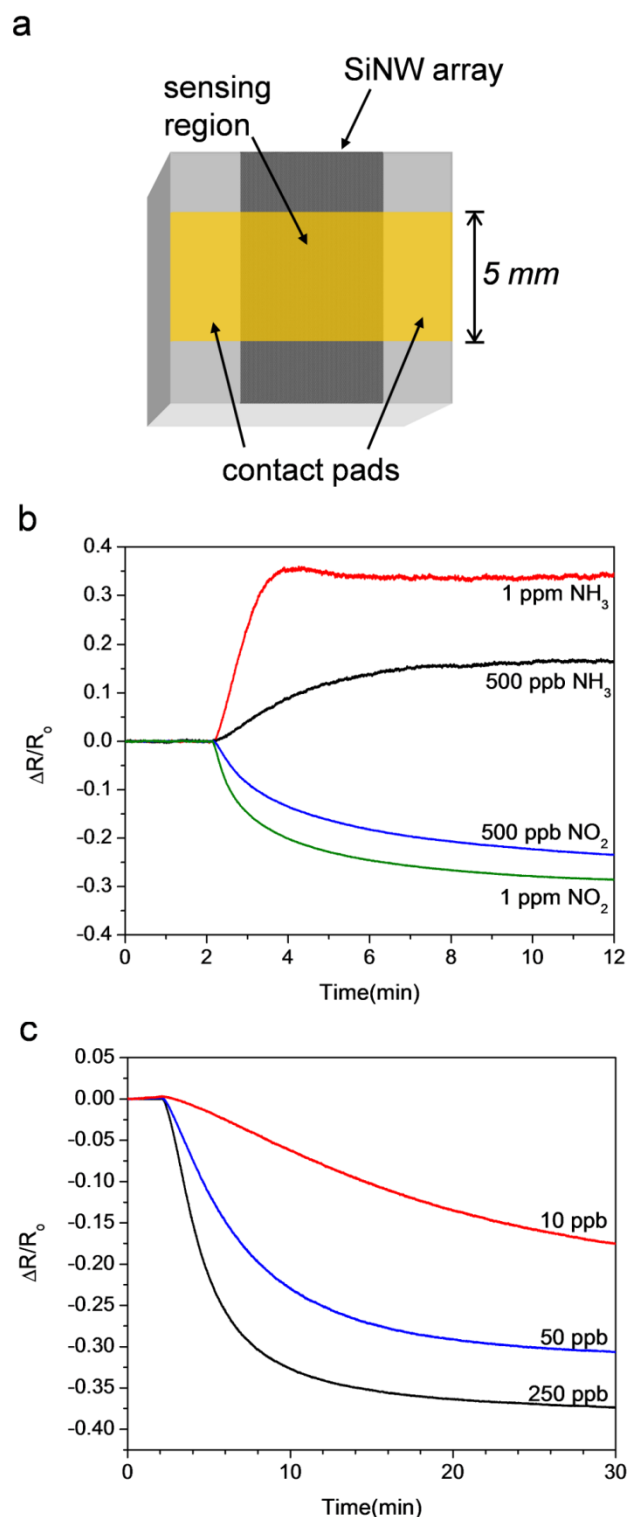


Figure 4. (a) Schematic diagram of completed device (top view). Sensor response to various concentrations of NO_2 and NH_3 following 2 min of clean air: (b) 1 ppm of NH_3 (red), 500 ppb of NH_3 (black), 1 ppm of NO_2 (green) and 500 ppb of NO_2 (blue) at $\sim 30\%$ RH; and (c) 250 ppb of NO_2 (black), 50 ppb of NO_2 (blue) and 10 ppb of NO_2 (red) at $<10\%$ RH.

typically etched for around 30 min to create up to $\sim 10^8$ vertical SiNWs that were 4–6 μm in length and $\sim 200 \text{ nm}$ in diameter, with a nanowire-to-nanowire distance of 490 nm. The initial

diameter of the polystyrene nanospheres defined the SiNW array's period while the combination of this initial diameter and subsequent etching of the nanospheres in oxygen plasma defined the resulting nanowire diameter. Next, a 500 nm thick layer of SiO₂ was evaporated over the entire device to electrically isolate the contact pad region from the bulk of the substrate. The oxide layer was then selectively etched away to reveal the SiNW array while removing any residual oxides on the nanowire surfaces. This step also decreased the contact resistance and established ohmic contact between the nanowire tips and the electrode layer deposited later. The entire SiNW array was then covered with a thick photoresist that was subsequently etched back in oxygen plasma to reveal just the SiNW tips (figures 2(e) and 3(e)).

After exposing the SiNW tips, a second layer of nanospheres identical to the ones used earlier in making the etch template was deposited. Since the period of this second nanosphere layer was equal to the period of the SiNWs, the new nanospheres were physically constrained to perfectly occupy the voids in the array and form a close-packed array on top of the exposed SiNW tips (figure 2(f)). After slightly etching down the second nanosphere array in an oxygen plasma (figures 2(g) and 3(f)), evaporating a metal electrode layer consisting of 20 nm thick titanium and 100 nm thick gold, and finally removing the photoresist and nanospheres with acetone (figure 2(h)), a large SiNW array (5 mm × 5 mm) with a PTE layer was formed as seen in figure 3(g). Some polystyrene nanospheres are still visible in figure 3(g) and are the result of local variations in photoresist and gold film thickness. In such cases, a more aggressive removal procedure, e.g. ultrasonication, may be required. The size and distribution of pores could be controlled by varying the nanosphere processing conditions, and the contact resistance between the nanowires and the top electrode could be reduced even further by performing a low-temperature anneal. The effect of pitch, density, diameter, doping and length on sensor performance is the focus of future and ongoing research. It may also be possible to further improve device sensitivity by fabricating silicon nanowires with a porous surface [12]. The completed devices were mounted on pin grid array (PGA) packages using a conductive epoxy to make the bottom electrical connections. Top electrical connections were made by wirebonding to the contact pads (figure 4(a)).

3. Results and discussion

To evaluate the chem/biosensing capabilities of our PTE SiNW array sensors, the completed devices were exposed to varying levels of NO₂ or NH₃ in a custom-built testing chamber. The specifics of the testing chamber and conditions have been described elsewhere [22]. Without further treatment or modification of silicon, surface adsorption of electron-withdrawing (donating) species like NO₂ (NH₃) decreases (increases) the overall resistance of our p-type Si devices. A significant distinction of our vapour delivery system is that it mixes the analytes of interest with humidified air as opposed to dry N₂ to simulate a real-world testing environment. Sensor

testing in humidified air is a crucial step towards real-world implementation because SiNWs are highly sensitive to water vapours [23, 24].

Our prototype sensors were tested for response to varying concentrations of NO₂ or NH₃ at a controlled temperature of 40 °C and relative humidity of ~30%. The change in resistance was determined by holding a constant current of 10 μA while recording voltage with a voltmeter. Sensor response was plotted as the change in resistance divided by the baseline resistance ($\Delta R/R_0$), without any filtering or smoothing of the raw, real-time data. Figure 4(b) shows the response of our prototype sensors to 1 ppm and 500 ppb of NO₂ and NH₃ in humidified air, respectively. As expected, total device resistance increased when exposed to NH₃ and decreased upon exposure to NO₂. The response reached saturation within a few minutes likely due to the PTE while the massively parallel nanowire configuration resulted in a very low noise profile. Humidified air adversely affects NO₂/NH₃ detection capabilities in metal oxide [25] and carbon nanotube [26] sensors. However, water appears to improve our sensor response at very low analyte concentrations, as will be detailed in a separate paper now in preparation. For detection at lower concentrations, the humidity level in the testing chamber was reduced to <10% RH. Sensor response following 30 min of exposure to 250, 50 and 10 ppb of NO₂ is shown in figure 4(c). For the lowest concentration level of 10 ppb, the sensor exhibited an 18% drop in resistance; 10 ppb sensitivity to NO₂ is among the lowest ever reported for an SiNW-based sensor and is far below various international and national requirement standards for annual NO₂ exposure [27].

The effect of the PTE on sensing performance was investigated by omitting the second nanosphere deposition step in the fabrication process to produce sensors with solid, non-porous electrodes. The devices with and without holes in the electrode layer were identical in all other aspects. The sensing response of both types of devices to 500 ppb of NH₃ is shown in figure 5. Both sensors reached similar saturation levels over time, but the PTE sensors, represented by the black line, reached this level in approximately 6 min. The non-porous variety, on the other hand, required almost 1 h to reach saturation. The response to NO₂ was also faster for the PTE sensors, albeit not as pronounced as with NH₃. This difference is explained by the parallel electrical configuration of the nanowires and the different resistance changes induced by the interacting molecules. NH₃ induces a resistance increase, so most of the nanowires must change for a large overall response by the array. In contrast, NO₂ decreases the individual nanowire resistance, so only a few nanowires can cause a large change in resistance for the entire array. For all detection schemes, but in particular for those resulting in increased nanowire resistance, the holes in the top electrode layer significantly improve detection response by allowing the analytes to flow directly through the electrode layer to quickly interact with all the nanowires in the array. The relative sensitivity to analyte electronegativity could be reversed by fabricating the nanowires from n-doped Si.

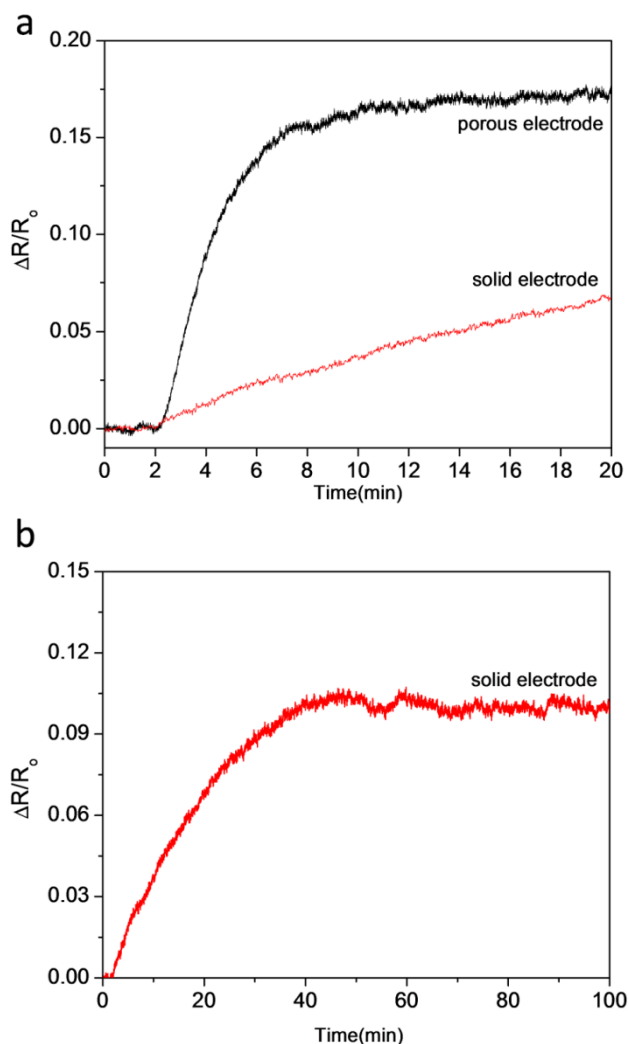


Figure 5. (a) PTE sensor (black) and solid electrode sensor (red) response to 500 ppb of NH₃ at ~30% RH. (b) The delayed saturation response of the solid electrode sensor.

4. Conclusion

In summary, highly sensitive detection of NO₂ and NH₃ was demonstrated using a silicon nanowire array sensor with a periodically porous top electrode (PTE). The flexible and widely applicable nanosphere-based fabrication process was used to successfully create gas sensors consisting of large arrays of vertical silicon nanowires without the use of time-intensive processes or specialised equipment. The PTE allowed consistent electrical connections to be made to each nanowire in the array while still allowing gases to freely flow through it. The resulting sensitivity and fast response times were among the best ever reported for SiNW sensors. By incorporating the vast collection of analyte-specific surface modification techniques that are currently available for SiNWs, we expect future devices to exhibit even greater sensitivity and selectivity towards a wide assortment of analytes.

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