Periodic microstructures fabricated by multiplex interfering femtosecond laser beams on graphene sheet

Yan Li

TEDA Applied Physics School,
Nankai University,
Tianjin, 300457, China
E-mail: lyfreework@126.com

Yudong Li*, Weike Shi, Shuqi Chen,
Guangzi Zhang, Zhibo Liu, Qian Sun and
Jianguo Tian

The Key Laboratory of Weak Light Non-linear Photonics,
Ministry of Education,
School of Physics,
Nankai University,
Tianjin, 300071, China
and
TEDA Applied Physics School,
Nankai University,
Tianjin, 300457, China
E-mail: yudongli@nankai.edu.cn
E-mail: xjshiweike@163.com
E-mail: schen@nankai.edu.cn
E-mail: photon1001@163.com
E-mail: rainingstar@nankai.edu.cn
E-mail: qiansun@nankai.edu.cn
E-mail: jjtian@nankai.edu.cn
*Corresponding author

Yanfei Xu and Yongsheng Chen

Nanoscale Science and Technology Centre,
Institute of Polymer Chemistry,
Nankai University,
Tianjin, 300071, China
E-mail: yanfeixu@mail.nankai.edu.cn
E-mail: yschen99@nankai.edu.cn

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Abstract: We fabricated successfully microstructures on graphene sheet by using multiplex interfering femtosecond laser beams. The symmetry, period and the fabrication depth are all influenced by the amount of interfering femtosecond beams. Using this method we fabricated grating-like microstructures and square lattice. In addition, we developed double-exposure technique with 2-beam interference and achieved square and rhombus lattice on graphene sheet.

Keywords: femtosecond laser beams; interference; grating; double-exposure; graphene sheet; periodic microstructures; nanomanufacturing.

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Biographical notes: Yan Li was a Master candidate in TEDA Applied Physics School, Nankai University during 2008 to 2011. After her graduation, she entered Pingdingshan University.

Yudong Li is a Professor in School of Physics, Nankai University.

Weike Shi is a Master candidate in TEDA Applied Physics School, Nankai University.

Shuqi Chen is an Assistant Professor in TEDA Applied Physics School, Nankai University.

Guangzi Zhang is a Master candidate in TEDA Applied Physics School, Nankai University.

Zhibo Liu is an Associate Professor in TEDA Applied Physics School, Nankai University.

Qian Sun is a Professor in School of Physics, Nankai University.

Jianguo Tian is a Professor in School of Physics, Nankai University.

Yanfei Xu is a Doctor candidate in Institute of Polymer Chemistry, Nankai University.

Yongsheng Chen is a Professor in Institute of Polymer Chemistry, Nankai University.

1 Introduction

Graphene is one of the most exciting research topics in recent years because of its remarkable electronic and mechanical properties (Li and Kaner, 2008; Geim and Novoselov, 2007). When micro- or nano-microstructures, such as nanoribbons, are patterned onto a graphene sheet, the energy band of the graphene can be opened and is decided by the structure characters (Han et al., 2007). It is worthy to study the techniques to introduce micro/nano structures onto the graphene surface. Research showed that many traditional micro-fabrication methods are sufficient for the patterning in graphene, such as mask lithography (Cong et al., 2009) and transfer printing (Liang et al., 2010).

Laser direct-writing method, in which the sample is exposed to laser beams, is a powerful and flexible fabrication method of microstructures. There are two methods to realise of laser direct-writing method. One is to focus the incident beam onto and scan across the sample surface. Zhou et al. (2010) wrote the channel and the square patterns on graphene surface by using continue wave from the diode laser. In order to fabricate complex patterns with higher resolution and smaller size, Zhang et al. (2010) used the femtosecond laser beams and succeeded in fabrication of curvilinear graphene oxide microcircuits. In this method, the focus of the incident laser beam should locate precisely at the graphene surface and the structures were fabricated point by point. It needs precise adjustment of the writing setup and long writing time. The other direct-writing method is to illuminate the sample by using interference pattern of multiplex laser beams. As long as the sample is located in the interfering region, microstructures can be written. Jia et al. (2008) fabricated two-dimensional (2D) microstructures in ZnO crystal surface by the interference of two femtosecond laser beams. Jia et al. (2009) produced complex periodic micro/nanostructure on 6H-SiC crystal with three femtosecond laser beams. And Kondo et al. (2003) got 2D periodic structures in negative photoresist SU-8.

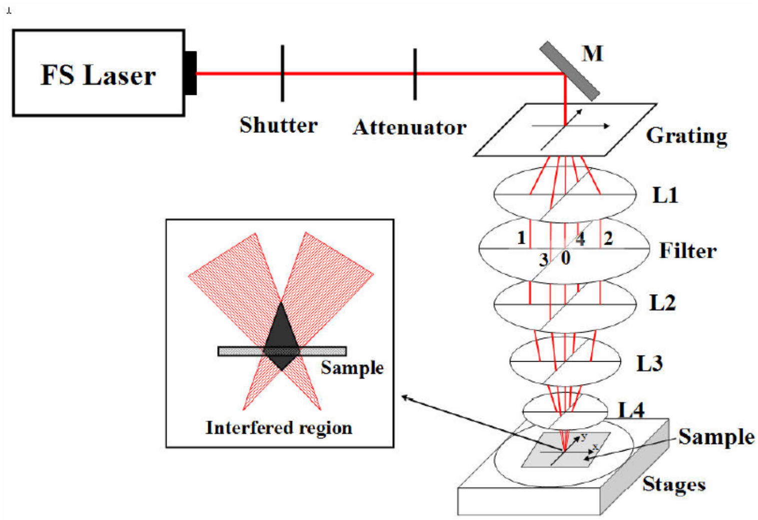
In this work, we fabricated 2D microstructures on graphene sheet by using interference of multiplex femtosecond beams. Grating-like and square microstructures were achieved successively on the graphene sheet. The structure characters, such as spatial symmetry, fabrication depth and period can be easily modulated in our method. With the double-exposure of the graphene sheet to the interference pattern, complex periodic microstructures can be written.

2 Experiment

In our experiments, the graphene sheet on a quartz substrate was produced by spin-coating graphene oxide solution on the quartz substrate and deoxygenating through exposure to hydrazine vapour and then annealing the sample in 1,000°C to render the material electrically conductive (Becerril et al., 2008). The thickness of the graphene sheet is less than 20 nanometers.

The experimental setup is shown in Figure 1, similar as the one used by Kondo et al. (2003). A femtosecond laser beam from an amplified Ti:sapphire system (Spectra Phys. Ltd, 800 nm, 120 fs, 1 kHz, horizontal polarisation) was incident perpendicular onto a diffraction grating and splitted into several beams by the diffraction of the grating. Lens L1 collimated the beams. Then the parallel beams were focused by lens set compounded by L2, L3 and L4. As analysed by Maznev et al. (1998), multiplex femtosecond laser beams will temporally overlap and interfere, as shown in the black region of the inset of Figure 1. When the graphene sheet is placed in the black region, interference pattern will illuminate graphene sheet. The focus lengths of L1 to L4 were 700 mm, 175 mm, 250 mm and 40 mm, respectively. The separation between L1 and L2 is 875 mm, 100 mm between L2 and L3, and 40 mm between L3 and L4. L3 and L4 make the diameter of overlapping region larger than 1.5 mm.

Figure 1 Schematic of experimental setup (see online version for colours)



Notes: L1, L2, L3 and L4: lenses; M: mirror; FS Laser: femtosecond laser. The inset shows the overlap of multiplex beams.

In our experiments, a one-dimensional grating (1DG) and a two-dimensional grating (2DG) were used to split the incident beam. In the following, beam 0 refers the transmitted beam and beams 1 to 4 refer to the diffracted beams. When the 1DG was used, the incident light was splitted into 3 beams. The graphene was illuminated by a 3-beam interference pattern which is produced by beams 0, 1 and 2. If the 2DG was used, 5-beam interference pattern were achieved by beams 0 to 5. Blocking the beam 0 by the filter in Figure 1, we can get 2-beam (beams 1 and 2) and 4-beam (beams 1 to 4) interference patterns.

Here 1DG and 2DG had the same spatial period, $\Lambda = 20$ μm. The gratings used in our experiment made the beams 1 to 4 had the same intensity, which was a quarter of beam 0. Because the incident beam was perpendicular to the grating, the diffraction beams, beams 1 to 4, were symmetric to the transmitted beam, beam 0. So the crossing angle between beam 0 and any of beams 1 to 4 in the air was constant, referred as θ in the following. According to grating equation and imagery theory, the incident femtosecond laser beams should be imaged on the plane about 12.3 mm beyond the lens L4. The graphene sheet was placed at this location in the following without special emphasis. And θ was about 16.7°.

3 Intensity distribution of interference pattern

Theoretically, the interference theory of plane waves was used (Hecht, 2002). The n-beam interference intensity distribution $I_n(\vec{r})$ can be calculated as following:

$$I_n(\vec{r}) = \left|\sum_i \tilde{U}_i(\vec{r})\right|^2 = \sum_i \tilde{U}_i(\vec{r}) \cdot \sum_i \tilde{U}_i^*(\vec{r}) \tag{1}$$

where $\tilde{U}_i(\vec{r})$ is the complex amplitude of i^{th} beam and can be written as

$$\tilde{U}_i(\vec{r}) = U_i^0 \exp\left[i\left(\vec{k}_i \cdot \vec{r} - \omega t + \phi_i\right)\right] \tag{2}$$

Here, n presents the amount of interfering beams, i the sequence number of the beams. U_i^0 is the amplitude of electric field and $U_1^0 = U_2^0 = U_3^0 = U_4^0 = U_0^0 / 2 = A$ in our experiment. $\vec{k}_i$, ω and ϕ_i are the wave vector, angular frequency and optical phase of i^{th} beam.

Without loss of generality, we assume t and ϕ_i in equation (2) are all 0. In order to make the interference pattern perpendicular to the graphene sheet surface, the incident beams must have symmetric geometry. So the interference pattern of 2 to 5 beams were produced by beams 1 and 2, beams 0 to 2, beams 1 to 4, and beams 0 to 4 respectively. Taking equation (2) into equation (1), we can get the intensity distributions of multi-beam interference on graphene sheet, i.e., the x-y plane shown in Figure 1:

$$I_2(x, y) = 4A^2 \cos^2(kx \sin\theta) \tag{3}$$

$$I_3(x, y) = 4A^2 \left[1 + \cos(kx \sin\theta)\right]^2 \tag{4}$$

$$I_4(x, y) = 4A^2 \left[\cos(kx \sin\theta) + \cos(ky \sin\theta)\right]^2 \tag{5}$$

$$I_5(x, y) = 4A^2 \left[1 + \cos(kx \sin\theta) + \cos(ky \sin\theta)\right]^2 \tag{6}$$

where $k = \dfrac{2\pi}{\lambda}$.

From equations (3) to (6), we can see that when the amount of the interfering beams changes, interference pattern varies greatly. The spatial symmetry and the period are different. 2-beam interference pattern is grating-like with the period of $\dfrac{\lambda}{2\sin\theta}$. 3-beam interference pattern is also grating-like. Because of the insert of beam 0 in the middle of beam 1 and 2, the grating space is $\dfrac{\lambda}{\sin\theta}$, double as the value for 2-beam interference. 4-beam interference pattern has square lattice with a rotation of 45° around the x axis in the x-y plane. The length of unit cell edge is $\dfrac{\lambda}{\sqrt{2}\sin\theta}$. And 5-beam interference pattern has centred rectangular unit cell with a length of unit cell edge of $\dfrac{\lambda}{\sin\theta}$.

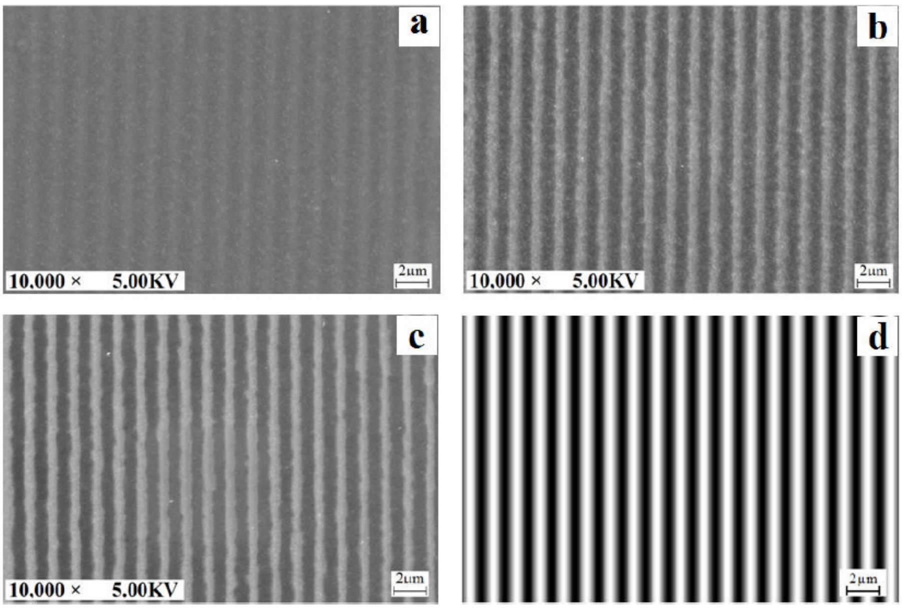
4 Results and discussions

4.1 Microstructure fabrication by using 2-beam interference

The grating-like periodic structures were fabricated on the graphene sheet surface by the illumination of 2-beam interference pattern. The energy of beams 1 and 2 was both

25 μJ/pulse. The exposure time was three minutes. The scanning electron microscope (SEM) images of periodic microribbons on the surface of graphene sheet are shown in Figure 2. The distance between the graphene sheet and L4 are 11.5 mm, 12.3 mm, and 13.0 mm for Figures 2(a) to 2(c), respectively. As a compare, the simulated intensity distribution of 2-beam interference pattern is shown as Figure 2(d). From Figure 2, it can be seen that microstructures are consistent with interference pattern. The period is about 1.4 μm, basically consistent with the theoretical value 1.39 μm. The fabricated grooves become deeper and the period becomes a little shorter when it increases the distance between the sample and L4. It can be explained by the optical path in the inset of Figure 1. With the increase in the distance, the beam intensity becomes higher, the angle θ becomes a little bit bigger.

Figure 2 The grating-like periodic structures fabricated by 2-beam interference



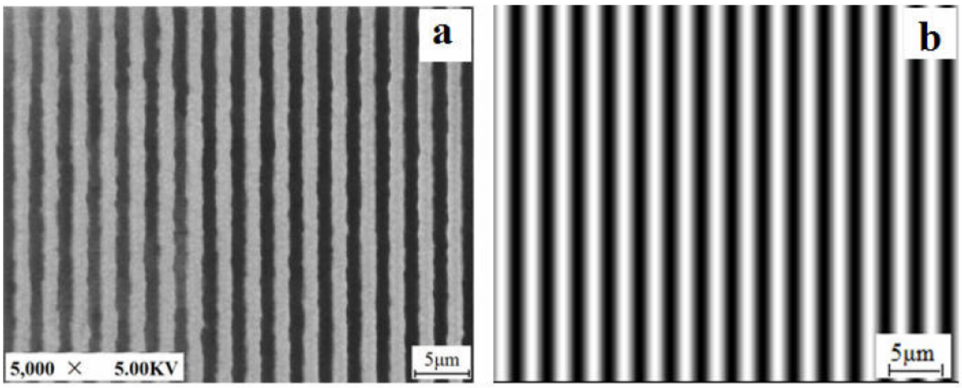
Notes: The distances between the graphene sheet and L4 are (a) 11.5 mm, (b) 12.3 mm, and (c) 13.0 mm, for a compare, (d) shows the simulated intensity distribution of 2-beam interference.

4.2 Microstructure fabrication by using 3-beam interference

Figure 3(a) shows the fabrication results by using 3-beam interference patterns. It is the grating-like periodic graphene microribbons, consistent with the interference pattern shown as Figure 3(b). Here both of beams 1 and 2 had the energy of 25 μJ/pulse, and beam 0 was of 100 μJ/pulse. The exposure time was three minutes. The distance between the sample and L4 was 12.3 mm. The period of the graphene microribbons in Figure 3(a) is about 2.8 μm, same as the theoretical value 2.78 μm. From Figure 3, it will be found that the grooves are deeper than the 2-beam interference cases shown in Figure 2.

According to equations (3) and (4), the maximum intensity of 3-beam interference pattern is four times of the value in 2-beam interference pattern under our experimental conditions. So 3-beam interference method is more suitable for the materials with high threshold writing intensity.

Figure 3 The grating-like periodic structures on graphene sheet fabricated by 3-beam interference, (a) SEM image of the ablation region (b) the simulated intensity distribution



4.3 Microstructure fabrication by using 4- and 5-beam interference

Figures 4 and 5 show the SEM images of the fabricated microstructure and the simulated intensity distribution of 4- and 5-beam interference on the surface of graphene sheet. Here the energies of beam 1 to 4 were of 6 μJ/pulse and beam 0 was of 24 μJ/pulse. The exposure times were four minutes for 4-beam and three minutes for 5-beam interference. We can see the length of unit cell edge is about 1.96 μm in Figure 4 and about 2.78 μm in Figure 5.

Figure 4 The square lattice structures on graphene sheet fabricated by 4-beam interference, (a) SEM images of the ablation region (b) the simulated intensity distribution

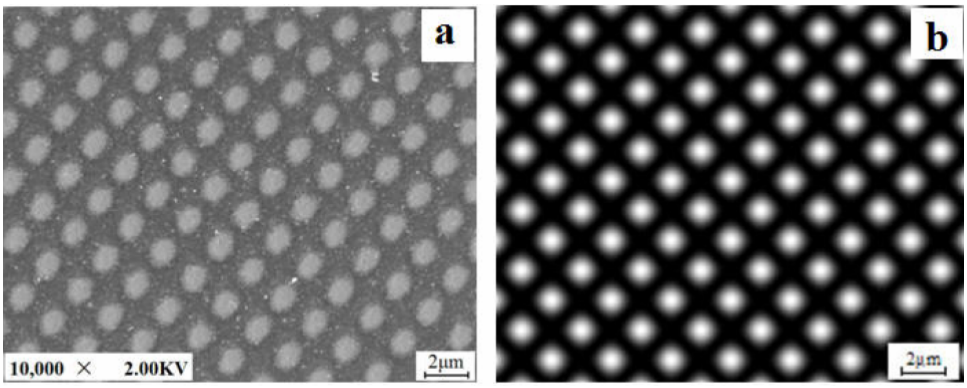
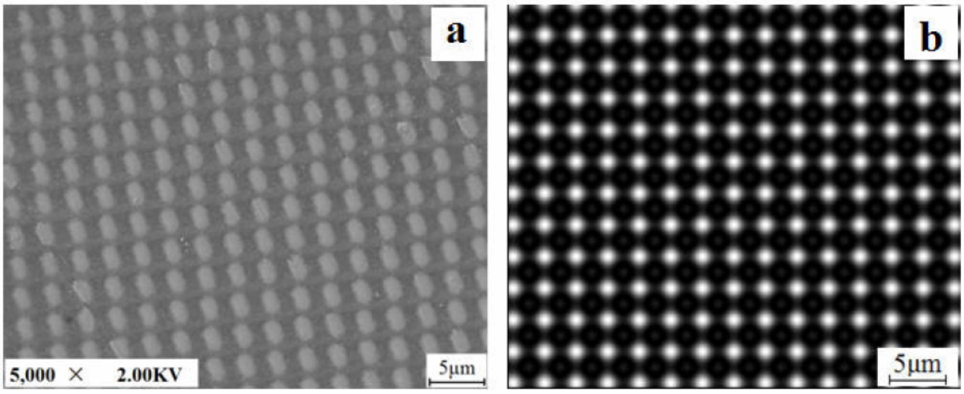


Figure 5 The square lattice structures on graphene sheet fabricated by 5-beam interference, (a) SEM image of the ablation area (b) the calculated intensity distribution



Although the intensity distribution of 5-beam interference pattern is centred rectangular as shown in Figure 5(b), the fabricated structure in Figure 5(a) has square unit cell. In fact, the intensity of the centre point of the unit cell of the interference pattern is far weaker than the intensity of the corner point of the unit cell, less than 1/10. Under our experiment conditions, the centre point is too weak to produce ablation. So it is square the microstructure fabricated by 5-beam interference. Same as the case for 3-beam interference method, fabrication depth of 5-beam interference method is larger than the depth of 4-beam interference method.

Theoretically, the intensity distribution of the interference pattern and hence the fabricated microstructures should be centrosymmetric. The experimental results show that the ablation pits look ellipsoidal in 4- and 5-beam interference methods. One reason is that, the diffraction efficiency of the 2DG is not uniform. So beams 1 to 4 have small differences in the intensity. If the intensities of beams 1 and 2 are higher than that of beams 3 and 4, the ablation pits is a little bit longer along x axis. Contrariwise, if beams 3 and 4 are stronger, the ablation pits become wider along y axis. Another reason is that the polarisations of the femtosecond laser beams are not exactly parallel to each other in their overlapping region. In our experiment, the polarisation direction of the laser beam before the diffraction grating is parallel to x axis. So the polarisation direction of beams 3 and 4 still parallels to x-axis. But polarisation directions of beams 1 and 2 deviate x-axis with an angle equal to θ. Therefore, the modulation of intensity is not 100%, which may also influence the quality of the periodic patterns (Su et al., 2003). The pits of structure will become wider. Because θ is only 16.7° in our experiments, the influence of the deviation in the polarisation direction is not obvious.

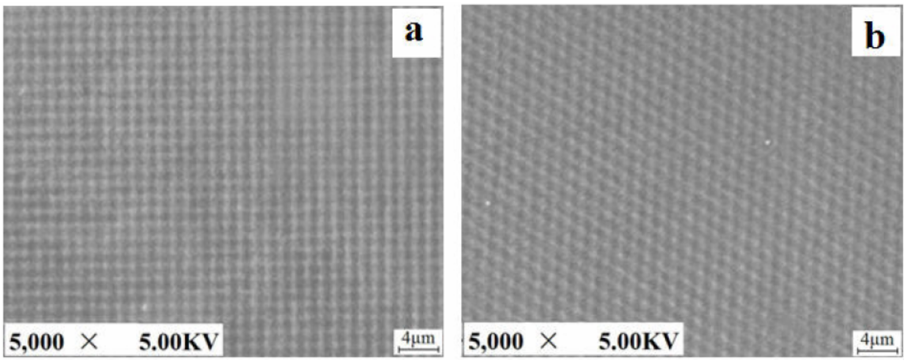
4.4 Double exposure of two beam interference

From the discussion above, we can see that 2-beam interference with the 1DG has many advantages over the multi-beam interference with 2DG, because the two first order diffraction beams from 1DG have the same polarisation direction and same intensity.

However, 2-beam interference from 1DG can only fabricate the grating-like, i.e., 1-dimensional periodic structures. In order to fabricate 2-dimensional periodic structures by using 2-beam interference with 1DG, we checked the double-exposure technique with 2-beam interference.

In double-exposure technique, the graphene sheet is exposed to the 2-beam interference pattern for certain time at first. Then after the sheet is rotated certain degree β in x-y plane, it is illuminated by the 2-beam interference pattern again. Figure 6 shows the SEM images of 2-dimensional periodic structures fabricated on the surface of graphene sheet by the double-exposure technique. The energy of beam 1 and 2 was 20 μJ/pulse and the exposure time was three minutes for each exposure. Figure 6(a) shows the square graphene microgrids obtained by double-exposure with rotating angle β of 90°. Figure 6(b) shows the rhombus graphene microgrids obtained by $\beta = 60°$. If the energies of interference beams are controlled carefully, more desired 2D microstructures can be obtained by multiplex rotation and exposure.

Figure 6 SEM images of microstructures fabricated on graphene sheet by double-exposure technique of 2-beam interference, (a) square lattice with rotation angle of 90°, and (b) rhombus lattice with rotation angle of 60°



5 Conclusions

In this work, multi-beam interference method of femtosecond laser light was used to fabricate microstructures on graphene sheet. The results show, grating-like periodic microstructures can be fabricated by 2- and 3-beam interference of femtosecond laser light, and 2-dimensional periodic microstructures with square lattice can be produced by 4- and 5-beam interference. With more interfering beams, we can achieve larger fabrication depth. In 4- and 5-beam interference method, the fabricated pits are dissymmetric. In order to improve the fabrication quality, we suggested a double-exposure technique with 2-beam interference pattern and succeeded in the production of square and rhombus lattice on graphene sheet. Multi-beam interference method provides a convenient efficient fabrication way of microstructures on graphene sheet.

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