X-ray investigations of buried high-temperature polymer nano dot gratings

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We present the results of time dependent x-ray scattering measurements during formation of a buried, modulated density structure below polymer film surface (DG) created at temperatures above the glass transition temperature $T_c$ during the thermal erasure of a holographically written surface relief grating (SRG). The surface relief gratings are initially formed on polymer films containing azobenzene side groups during pulse-like exposure with a holographic pattern of circularly polarized light at 488nm. The material gives a mechanical response to the actinic light forming a sinusoidal surface pattern in a one-step process. Theoretical predictions show that SRG formation is accompanied by a density grating just below the film surface. Upon annealing above polymers glass transition temperature the SRG melts while some of the density modulation in the bulky volume remains and a non-sinusoidal DG is rebuilt after long term annealing at $T > T_c$ of approx. 30 K. The re-induction of density volume structure is assisted by red laser light exposure of the film upon annealing. The observed homopolymer pDR1m was found to be the most effective material to build the modulated buried DG. This might be due to the formation of light aligned homeotropic clusters below former SRG peak positions.

We already reported about density grating formation in one-dimensional line gratings [1-3]. Now, we produced cross-written zero-dimensional nano dot gratings also. Depending on inscription process we manufactured $60^\circ$ and $90^\circ$ dot gratings with a period of 880 nm each upon laser inscription times from 1…10 min at 100 mW/cm$^2$ (see fig.1a). Long term heating of the light induced polymer surface relief gratings (SRG) above the glass transition temperature completely flattens the surface profile [1]. In previous investigations we found the formation of a buried, modulated density grating (DG) below the surface for azobenzene homopolymer (pDR1M) one-dimensional line gratings. We recently reported [4-6] about x-ray specular and diffuse scattering investigations of azobenzene polymer surface line gratings as one-dimensional nanostructures produced by holographic inscription. Consequently, we produced cross-written nano dot gratings also. Depending on inscription process we manufactured $60^\circ$ and $90^\circ$ dot gratings with a period of 880 nm each upon laser inscription times from 1…10 min at 100 mW/cm$^2$. A nano dot patterned sample was mounted on a heating stage (BW2, E=10 keV, horizontal set up, Cyberstar scintillation counter with analyser crystal) using angles of incidence $\alpha_i$ of 0.2…1.5°. The intensities of the $\pm 1^{st}$ and $\pm 2^{nd}$ order x-ray grating peaks and the $1^{st}$ order VIS scattering peak were detected for linearly rising temperature (fig 1b, courtesy of picture: Andreas Pucher). As expected, both x-ray and VIS scattered intensity vanish close to $T_c$, but both signals reappear upon continued heating at 160°C (fig 2a 2d-map: reddish colours correspond to high grating peak as well as specular intensities, blue line represents $1^{st}$ scattered order of VIS light). As seen in fig 2b the grating region has been flattened while the position of the red laser beam striking the sample is now designated by a photo bleached region (PBR). This behaviour might be due to the formation of H-aggregates [7] amongst the azobenzene groups, which results in a blue shift of absorption yielding the yellowish colouring. Moreover, as proved by AFM, the entire nano dot grating has been transformed into a line grating again. This transition from zero- to one-dimensional nanostructure is not yet finally understood.

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Figure 1: Left (a): AFM topography of cross-written nano dot gratings (azobenzene homopolymer pDR1M [1], D=880 nm, 60° dots, h=79, inscription time 5 min at writing laser power density of 100 mW/cm² at 488 nm writing beam wavelength; right (b): Experimental set up at BW2

Figure 2: left (a): 2d-q, Scans for erasure of SRG and formation of a high temperature DG for pDR1M with same periodicity above T_G (specular condition at 1/D=0, grating peaks ±1”and ±2” nano dot grating order; blue line: development of VIS 1” scattered order, He-Ne-laser 633 nm); Picture and AFM topography of nano dot grating before (upper right (b)) and after (lower right (c)) high temperature treatment under red laser illumination

References

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