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Absorptive structures fabricated by laser writing

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The spectral properties of metallic surfaces are of much interest in applications such as solar absorption. These may help improve the performance of solar thermal systems and solar cells. The fabrication of periodic metallic features on the device surface is known to increase absorption and the use of diffractive structures has been reported. In this paper we report use of corrugated metal structures formed by a novel approach. Two photon polymerisation is used to write a 2D grid pattern, with a pitch of either 2 or 3 microns, onto which a chrome metal layer was evaporated. A Ti:sapphire laser, with wavelength 795 nm, 80MHz repetition rate, 100 fs pulse duration and an average power of 700 mW, was used to write the grid in a Zr-loaded sol-gel. The measured reflection and transmission properties show that the absorption increases in a part of the spectrum that can be related to the structure's dimensions. A RCWA code was used to define the optimal parameters for solar absorption in this system.

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1. Introduction

There is much interest in developing solar absorbers for solar thermal systems [1]. There are several approaches to this all with the aim of achieving high solar absorbance and low thermal emittance. In some cases the ability to withstand harsh environmental conditions (e.g. heat) is also a requirement. Typically the requirement is for a low reflectance at wavelengths $\leq 3\mu m$ and a high reflectance at longer wavelengths.

Several approaches are under investigation both in materials and surface engineering. The intrinsic properties of a suitable material can be utilised but it is difficult to find a material that covers the entire solar region of interest. Multilayer absorbers [2, 3] and dielectric coatings [4] improve on this by building a metal/dielectric multilayer stack to give an interference effect in the absorber. Semiconductor-metal tandems and selectively solar-transmitting coatings work by using a strongly absorbing coating to a substrate.

An alternative technique is to use surface texturing [5]. With careful design the surfaces will absorb solar energy while appearing highly reflective to thermal energy. The emittance can be adjusted by modifying the microstructure. These structures can be grooves, needles, pores or simply roughened surfaces.

Periodic grating-like structures are particularly attractive [6, 7] since they are straight forward to fabricate, the reproducibility is good and, by using embossing techniques, it is feasible to fabricate them over large areas. Studies have been made on one-dimensional (1D) and two-dimensional (2D) surface relief gratings fabricated in metals such as tungsten. In order to fabricate the structures, fast atom beam etching techniques have been used. For this process a mask of anodic porous alumina was used as the template for patterning.

In this paper we describe an alternative approach to fabricating a surface for increased solar absorbance using two-photon polymerisation (2PP) to write a high aspect ratio template over which a thin metal coating is applied. Over recent years, 2PP has established itself as a technique for micro and nano-scale rapid prototyping [8 - 10] and complex shapes such as micro-models, woodpile photonic structures and spiral structures have been realized in several material systems: sol-gels, organically modified ceramics and resins [8, 10-12]. Of direct relevance to this study, previous work has demonstrated that the 2PP technique can form 2D grating patterns for use in photonic applications such as plasmonic structures [13]. In this report grid structures with sub-micron heights were used in a lift-off process to define gold islands that showed transmission properties modified by the periodic structure. In a second study [14], the laser writing beam was modified using an axicon lens to generate a high aspect ratio Bessel beam. This Bessel region caused the 2PP process to be extended in depth over several microns and obviated the need for repeat writing to build up high-walled structures.

2PP is a rapid prototyping technique that can easily create defined (as opposed to random) test structures for evaluation whereas the other techniques listed above are less versatile. In the following sections the writing of 2D grating structures with period of 2 and 3 μm will be described. Their absorption properties, when coated with a thin chromium layer are shown to be significantly modified by the structure as compared to a plane thin film. The spectroscopic measurements are in agreement with rigorous coupled wave analysis (RCWA) predictions.

2. Experimental

The experimental setup has been described previously [14] and comprises a beam expanded Ti: sapphire laser (wavelength 795nm, 100fs pulse width, 80MHz pulse repetition rate, average power 700mW), axicon (base angle of 0.5 degree) and a focussing objective (NA=1.25, ×100, f=1.6mm). Laser power is adjusted by inserting neutral density filters and switched by a shutter. A CCD camera is used as an on-line monitor for the interaction process and the processing powers are measured after the objective.

Fig. 1 shows a schematic diagram of the optical layout of the axicon modified beam. It shows how two features are formed in the region behind the focus of the microscope objective. The feature of interest in this paper is the long Bessel beam formed by the axicon. In this way high aspect ratio lines can be formed in the resin.

The structures were written in sol-gel resin [12]. Briefly, a precursor containing 5 mol% Zr was prepared by hydrolysis of an organo-silane to which a chelated zirconium alkoxide was added. Condensation reactions were promoted between the hydrolyzed precursors by the addition of water. Finally the photo-initiator (2.0% by weight) 4,4′-bis(diethylamino) benzophenone was added.

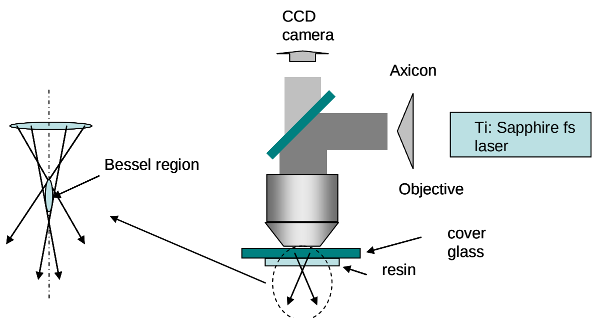


Fig. 1. Two-photon polymerisation scheme with a Bessel beam.

Zr loaded resin was spun onto glass substrate (thickness 170 μm) to give resin thicknesses in the range 1 – 8 μm, then placed inverted onto the motorized XYZ stages, which control the fabrication process. A layer of index matching fluid is used between the objective and the substrate. Isopropyl alcohol is used to develop the sample after exposure and the remaining polymerised structures are examined under a SEM (Hitachi S4000).

The objective in this investigation was to write grid structures with a range of heights for the two periods of interest. Periods of 2 and 3 μm were chosen to give increased absorption in the solar region and it is interesting to see the effect of changing the grid structure on the spectrum. Because the Bessel region is elongated, and longer than the thickness of the resin, the height of the grid pattern is defined by the resin thickness. The width of the line structures is controlled by the exposure: i.e. a combination of scanning speed and laser power.

In the final fabrication step a 200nm thick chromium layer was evaporated onto the structure using a Temscal vacuum evaporator.

The height and width of the coated samples were characterized using a SEM (Hitachi 2000) and the reflectance spectra measured over the range 0.3 – 5 μm using a Bruker IFS66/S Fourier transform infrared (FTIR) interferometer.

3. Results

The reflectivity of thin (200nm) film chromium is reported as being 70 – 80 % in the 0.5 – 2.5 μm region of the solar spectrum and the effect of introducing a grating structure to the film was simulated using a RCWA code (Unigit). The design of the structure is shown schematically in Figure 2 and is a typical two-dimensional grid structure used for solar-grating absorption. In the simulation two grating periods: 2 and 3 μm were investigated. The width of the lines was set at 400 nm as this was typical of what was achievable in the 2PP experiment. This gave a width to period ratio of 0.2 and 0.13 for the 2 and 3 micron period gratings respectively. A 200 nm layer of chromium is assumed to coat the top and bottom layers of the structure but not the side walls.

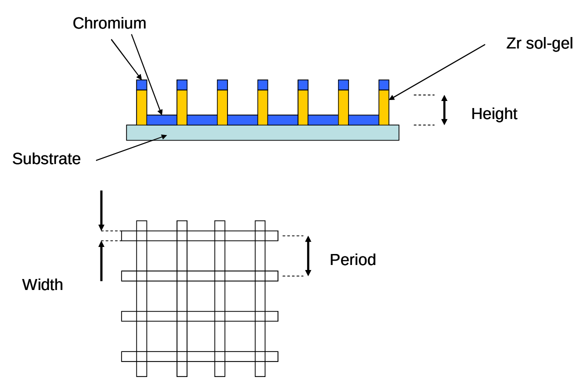
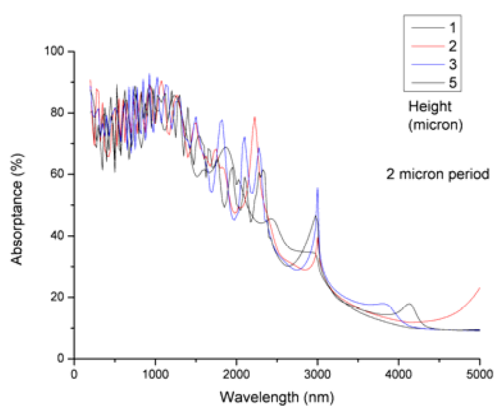
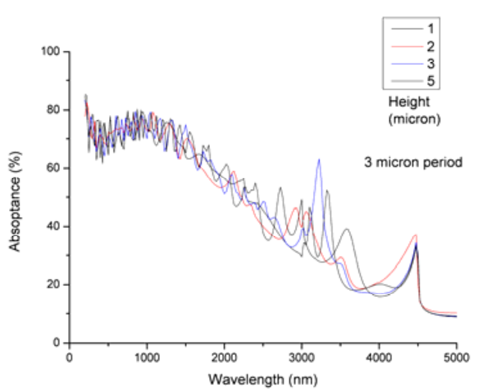


Fig. 2. Design of the grating structure.

The effect of the structure height was also investigated for a typical range values achievable by the axicon modified 2PP writing technique (1-5 μm). Figure 3 shows the effect of varying the height of the structure for each period on the absorptance of the chromium in the spectral range 0.3 – 5 μm. The Unigit code predicts reflection (R) and the absorption is assumed to be (1-R). Fig. 3a shows the predictions for the 2 μm periods structure and 3b the 3 μm period. Interestingly the overall form of the curves is seen to be insensitive to height and only the detail of the absorption spectrum changes significantly.



a



b

Fig. 3. RCWA simulation of absorptance in the grating structure, a) 2 micron period, b) 3 micron period.

Typically, the terrestrial solar spectrum peaks at approximately 0.5 μm and is quasi black body falling to 10 % at approximately 2.0 μm [15]. Therefore any increase in absorbance in this wavelength range is useful for solar trapping applications. The simulation also predicted zero transmission in the region shown in Figure 3. So the non-reflected radiation can be assumed to be absorbed. If the reflection spectra for the grating structure are compared with the unstructured thin film reflection, then a significant increase in absorption is seen over the 0.3 – 2.0 μm range.

In order to realise the structures experimentally, the cross pattern was written in the Zr-loaded sol-gel material using the system in Figure 1. A range of writing speeds was used (80 to 150 μm s^{-1}) and laser powers of 93 and 70 mW. The area of the structures was 100 x 100 μm^2. It was found from previous studies that the effect on the width of the lines was minimal over this range [14]. In order to avoid polymerisation at the annulus plane of the Bessel beam, the focus of the objective was set outside of the sol-gel. This reduced the potential length of the long polymerisation region but a regime was found that still allowed the control of feature height over the range of interest 1 – 5 μm.

After the writing phase, the structures were washed in alcohol to remove the uncured sol-gel before drying in air. A 200 nm layer of chromium metal was subsequently evaporated onto the structures.

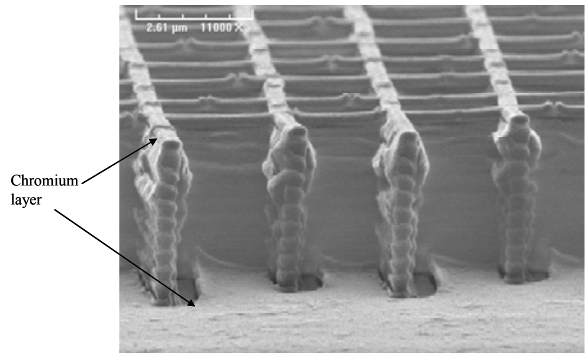
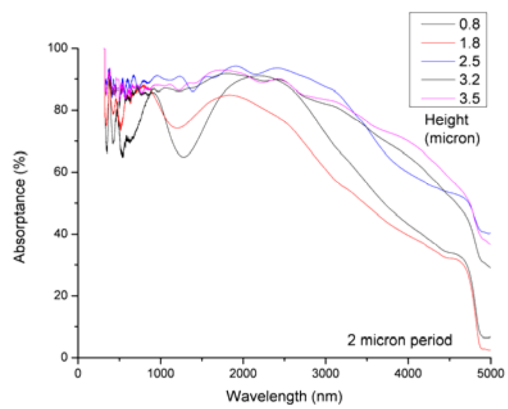


Fig. 4. Laser written structure

Fig. 4 shows a typical polymer templated structure after chromium coating. The period in this case is 3 μm and the height 3.8 μm. The writing process extended the lines so that the cross-section can clearly be seen.



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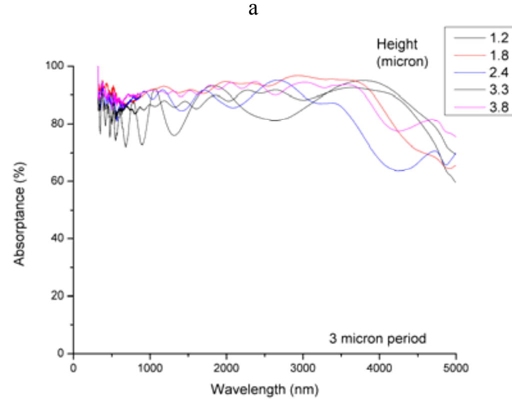

b

Fig. 5. Absorptance measurements for the Cr coated laser written structure, a) 2 micron period, b) 3 micron period

The absorption spectra are shown in Fig. 5, calculated from the measured reflectance spectra assuming zero transmission, for representative grating heights in the range nominally 1 – 4 μm. The measurements show that the absorption is indeed higher with a grating structure. In the case of the 2 μm period structure (Figure 5a) the absorptance increases to approximately 80% and similarly in Fig. 5b (the 3μm period structure) the absorptance is again around 80% over the region of solar interest. In the case of the 2 micron structure, the general trend is for the absorptance to decrease rapidly at wavelengths above 2 μm. This long wavelength decrease is mainly due to an increase in reflectivity and implies a low thermal emittance, in this region, and this is desirable in a good solar absorber. The change in period from 2 – 3 μm gives marked differences in the spectra as do differences in structure height. This is probably due to the fact that the basis of this phenomenon is interference and changes on a scale comparable to the wavelengths involved will cause significant changes. Note the signal-to-noise ratio at short wavelengths reduces the accuracy of the data below 700 nm.

Comparing Fig. 5 to Fig. 3, there is broad agreement but the measured absorptances appear higher than the prediction. The absorptance is probably slightly over estimated as the reflection data was referenced to a reflector. Also absorptance is predicted to fall at the longer wavelengths starting at approximately 1 μm. In the measured spectra (Fig. 5) this fall occurs at longer wavelengths. This may be caused by imperfections in the polymer structure. Unfortunately the UNIGIT code is designed for idealised periodic structures and does not allow the introduction of random imperfections and so this could not be simulated in our investigation. As shown in Figure 4, there is some statistical variation in the grating period caused by inaccuracy in the stage resolution and also the side walls show non-ideal features such as the fine periodic structure in the vertical direction.

4. Conclusions

In conclusion it is demonstrated that 2PP is a viable technique for the rapid fabrication of templates for diffractive solar absorption enhancement. Two-dimensional periodic structures were written, in a Zr-loaded sol-gel, and coated with chromium metal to enhance the absorption of the system as compared to a plane surface. In a final device, the structure could be fabricated by low–cost, high-volume processes such as embossing. The 2PP technique allows rapid prototyping of candidate structures for evaluation.

The Bessel beam was used to polymerize sol-gel films of different thicknesses. Reflection and transmission measurements were made, for the different structure heights, over a spectral range 0.3 – 5 μm. and the absorption calculated.

A RCWA code was used to predict the reflection/absorption behaviour and was in broad agreement with the experimental measurements.

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