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Enhancement of photocatalytic activity by femtosecond-laser induced periodic surface structures of Si

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Abstract: Laser induced periodic surface structures (LIPSS) represent a kind of top down approach to produce highly reproducible nano/microstructures without going for any sophisticated process of lithography. This method is much simpler and cost effective. In this work, LIPSS on Si surfaces were generated using femtosecond laser pulses of 800 nm wavelength. Photocatalytic substrates were prepared by depositing TiO_2 thin films on top of the structured and unstructured Si wafer. The coatings were produced by sputtering from a Ti target in two different types of oxygen atmospheres. In first case, the oxygen pressure within the sputtering chamber was chosen to be high (3×10^{-2} mbar) whereas it was one order of magnitude lower in second case (2.1×10^{-3} mbar). In photocatalytic dye decomposition study of Methylene blue dye it was found that in the presence of LIPSS the activity can be enhanced by 2.1 and 3.3 times with high pressure and low pressure grown TiO_2 thin films, respectively. The increase in photocatalytic activity is attributed to the enlargement of effective surface area. In comparative study, the dye decomposition rates of TiO_2 thin films grown on LIPSS are found to be much higher than the value for standard reference thin film material Pilkington Activ™.

Key words: laser induced periodic surface structures; nanoripples; silicon; photocatalytic dye decomposition; TiO_2 thin film; femtosecond laser pulses

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1. Introduction

The generation of laser induced periodic surface structures (LIPSS) represents a particular kind of top down approach to produce highly reproducible nano/microstructures without going for any sophisticated process of lithography. This method is much simpler and cost effective but comes along with a certain degree of randomness in the geometry of the structures. In many cases, however, the aspect of randomness can be well tolerated. Therefore, LIPSS and related structures have been used for various applications such as surface enhanced Raman spectroscopy (SERS), colorization of metals, enhancement of emission efficiency of incandescent light sources, tribology, efficient photoelectron emission, realization of efficient photovoltaic cell and LED, optical memory and controlling hydrophobic properties of materials etc.[1–13]. Dyes are the waste products of various industries like textile, leather, plastic, pharmaceutical, or paper. These dyes generally cause serious water pollution. Currently, heterogeneous ultraviolet (UV) photocatalytic dye decomposition with semiconductor nanostructures is one of the best established methods for removal of these dyes[14, 15]. Here we report on the use of LIPSS generated on Si (SiLIPSS) for enhanced photocatalytic dye decomposition activity. Discussion is given for the cause of this enhancement and its significance with respect to the already reported methods. A comparison of the performance of the grown samples was carried out with respect to the standard reference material Pilkington Activ™.

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2. Experimental details

2.1. Photocatalytic substrate preparation

Photocatalytically active films were prepared by deposition of TiO_2 onto the SiLIPSS using a magnetron sputtering system. The SiLIPSS were prepared with linearly polarized femtosecond (fs) laser pulses at a central wavelength of 800 nm emitted from an amplified Ti:sapphire laser system (Spitfire, Spectra Physics). The duration and repetition rate of the laser pulses were 120 fs and 1 kHz, respectively. The samples were fixed on a computer controlled two-axis translation stage (MFA-CC stages, Newport) in the focal plane of a cylindrical lens (focal length $f = 100$ mm) for the laser processing. The produced line focus had an extension of $100 \times 12\,000$ μm^2. The samples were moved by raster scanning with a velocity of 0.5 mm/s across this line focus to generate LIPSS in an area of 2×2 cm^2. All the experiments were carried out in air environment. The LIPSS were characterized using a field-emission scanning electron microscope (FESEM, JEOL JSM-6400F). The FESEM image of the SiLIPSS is shown in Fig. 1(a).

These SiLIPSS were generated under optimized working conditions (pulse energy 0.3 mJ, velocity 0.5 mm/s). The orientation of SiLIPSS were found to be perpendicular to the polarization of the laser beam (shown as double sided arrow in Fig. 1(a)). In order to quantitatively estimate the period of

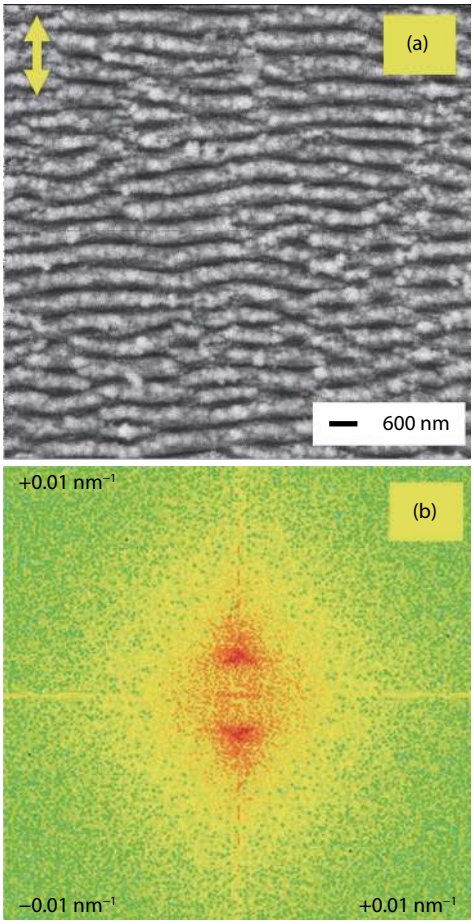

Fig. 1. (Color online) (a) FESEM images of SiLIPSS (double sided arrow : polarization direction of laser pulses). (b) Related spatial frequency map obtained by 2D-FFT.

these SiLIPSS the two-dimensional fast Fourier transform (2D-FFT) analysis of their FESEM image was done by using ImageJ software. From this 2D-FFT analysis (Fig. 1(b)), the period was estimated to be around 500 nm.

The details of the growth conditions for the TiO_2 thin films were discussed in a previous publication[16]. Briefly summarized, TiO_2 thin films were grown by sputtering material from a Ti target in two different oxygen atmospheres. In the first case, the oxygen pressure was chosen to be high (3×10^{-2} mbar) in the sputtering chamber. In the second case, the oxygen pressure was one order of magnitude lower (2.1×10^{-3} mbar). These types of thin films will be referred to as high pressure grown TiO_2 thin films ($HPTiO_2$) and low pressure grown TiO_2 thin films ($LPTiO_2$), respectively. The deposition time of the thin films was 90 min for the $HPTiO_2$ and 70 min for the $LPTiO_2$ to obtain nearly comparable film thicknesses of about 180 nm and 145 nm, respectively. To enable a comparison to a reference surface, TiO_2 thin films were also deposited onto Si containing no LIPSS (NoLIPSS). The details about these samples are given in Table 1.

2.2. Photocatalytic dye decomposition study

A reactor consisting of a UV light source (Philips CLEO Professional 140W-R, UVA-power app. 21 mW/cm^2) with a mounted-in magnetic stirrer system was used for photocatalytic induced dye decomposition studies. For this aqueous solution of methylene blue (MB) dye (0.01 mmol/L) was taken as a test medium. The coated samples were put in a solution filled

Table 1. Nomenclature and description of samples.

Name of sample	Details of sample
$HPTiO_2$-SiLIPSS	High pressure grown TiO_2 thin film on Si surface containing LIPSS
$HPTiO_2$-NoLIPSS	High pressure grown TiO_2 thin film on Si surface containing no LIPSS
$LPTiO_2$-SiLIPSS	Low pressure grown TiO_2 thin film on Si surface containing LIPSS
$LPTiO_2$-NoLIPSS	Low pressure grown TiO_2 thin film on Si surface containing no LIPSS

beaker (30 ml) and closed by a quartz plate to prevent solution evaporation. The distance between the test sample and the light source was about 32 cm. Prior to light irradiation, the solution was kept for 30 min in dark condition for complete adsorption-desorption of dyes on the catalyst surface. Thereafter, the samples were irradiated with UV light for the photocatalytic reaction. The whole photoreaction (dark as well light exposure condition) was carried out under continuous slow stirring. To ensure reproducibility and comparability, the experimental conditions were kept the same for all the samples. The MB dye decomposition was measured over a whole irradiation time of four hours by using UV-visible absorption spectroscopy of the solution (Perkin Elmer Lambda 2) comparing the intensities at a wavelength of 664 nm. For comparison, the photocatalysis at the same conditions was carried out with standard Pilkington Activ^{TM} reference glass samples.

3. Results and discussion

3.1. Film structure

The influence of oxygen partial pressure during film deposition on the film structure was investigated by X-ray diffraction (XRD) measurements (Siemens D5000 diffractometer with Cu Kα radiation and a detector scan with an incidence angle of 1°)[17]. These investigations revealed a strong dependence of the appearance of the TiO_2 phase on oxygen partial pressure. So, the XRD investigations of the TiO_2 layers deposited at low sputtering pressure identified both rutile and anatase phases but layers deposited at pressures above 4×10^{-3} mbar showed only anatase reflection peaks. Until the critical value of about 4×10^{-3} mbar, where rutile and anatase are formed, the XRD peak-intensities for both TiO_2 modifications decreased. But above this value, the intensity of the anatase (101) peak increased strongly with higher sputtering pressure.

3.2. Photocatalytic activity for high pressure grown TiO_2 samples, $HPTiO_2$-SiLIPSS and $HPTiO_2$-NoLIPSS

Fig. 2 shows the UV photocatalytic degradation of MB dye (plot of C/C_0 versus time) with high pressure grown TiO_2 thin films on Si surface containg LIPSS ($HPTiO_2$-SiLIPSS) and no LIPSS ($HPTiO_2$-NoLIPSS). Here, C_0 is the initial concentration of aqueous solution of MB dye and C is its concentration after a certain time of photocatalytic reaction. As can be seen from this figure, the MB dye reduces to about 8% of its initial concentration after 4 h of photocatalytic activity for $HPTiO_2$-SiLIPSS sample whereas it is 30% for $HPTiO_2$-NoLIPSS samples. The corresponding values of MB dye degradation efficiency $[(C_0 - C)/C_0 \times 100]$ are 92% and 70% for $HPTiO_2$-SiLIPSS and $HPTiO_2$-NoLIPSS, respectively. This clearly in-

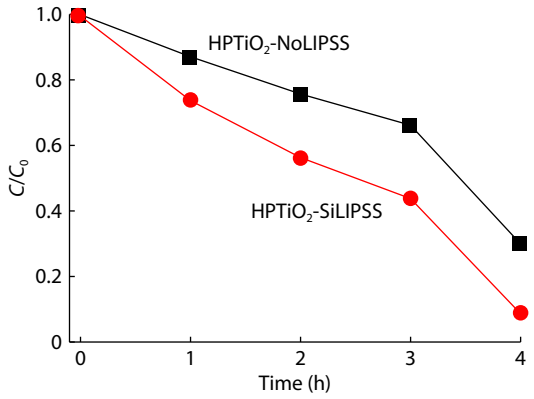

Fig. 2. (Color online) UV photocatalytic degradation of MB dye (plot of C/C_0 versus time) with high pressure grown TiO_2 thin films grown on Si substrate containing LIPSS ($HPTiO_2$-SiLIPSS, quadratic symbols) and no LIPSS ($HPTiO_2$-NoLIPSS, circles).

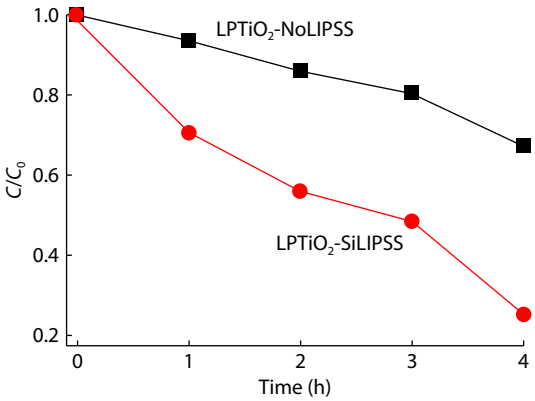

Fig. 3. (Color online) UV photocatalytic degradation of MB dye (plot of C/C_0 versus time) with low pressure grown TiO_2 thin films grown on Si substrate containing LIPSS ($LPTiO_2$-SiLIPSS, quadratic symbols) and no LIPSS ($LPTiO_2$-NoLIPSS, circles).

dicates that the SiLIPSS played an important role in the enhancement of the photocatalytic dye decomposition activity.

3.3. Photocatalytic activity for low pressure grown TiO_2 samples, $LPTiO_2$-SiLIPSS and $LPTiO_2$-NoLIPSS

Fig. 3 shows the C/C_0 versus time plot for MB dye decomposition with low pressure grown TiO_2 thin films on Si surface containing LIPSS ($LPTiO_2$-SiLIPSS) and no LIPSS ($LPTiO_2$-NoLIPSS).

As can be seen from this figure, the MB dye content reduces to about 25% of its initial concentration after 4 h of photocatalytic activity with the $LPTiO_2$-SiLIPSS sample whereas with $LPTiO_2$-NoLIPSS it is 70%. In this case, the dye decomposition efficiencies are found to be 75% and 30% respectively for $LPTiO_2$-SiLIPSS and $LPTiO_2$-NoLIPSS respectively. So, this again indicates that the SiLIPSS played an important role in enhancement of the photocatalytic dye decomposition activity.

3.4. Evaluation of enhancement of photocatalytic activity in terms of reaction rate constant

The reaction rate constant (k) is a kind of figure of merit parameter in order to quantitatively express the photocatalytic activity of the materials. In order to know further details of the enhancement of the photocatalytic activity due to LIPSS we estimated the reaction rate constants of the various

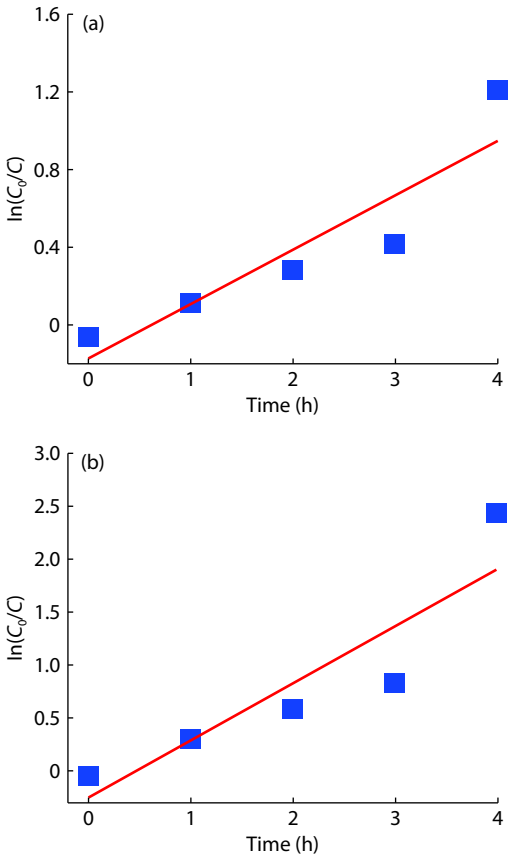

Fig. 4. (Color online) $\ln(C_0/C)$ versus photocatalysis time graph for high pressure grown TiO_2 thin film on Si substrate containing no LIPSS ($HPTiO_2$-NoLIPSS) and LIPSS ($HPTiO_2$-SiLIPSS).

Table 2. Reaction rate constants of high pressure grown TiO_2 thin film on Si substrate containing no LIPSS ($HPTiO_2$-NoLIPSS) and LIPSS ($HPTiO_2$-SiLIPSS).

Name of sample	k (h^{-1})	Enhancement factor
$HPTiO_2$-NoLIPSS	0.26	2.1
$HPTiO_2$-SiLIPSS	0.54	

samples by following the standard procedure. In brief, to estimate this parameter first a graph between $\ln(C_0/C)$ versus photocatalysis time (t) was drawn. Thereafter considering the pseudo-first kinetics, a linear fit line obeying the equation $\ln(C_0/C) = kt$ was drawn for this graph. The slope of this linear fit line provided us the reaction constant k.

The $\ln(C_0/C)$ versus photocatalysis time graph for high pressure grown TiO_2 thin films, $HPTiO_2$-NoLIPSS and $HPTiO_2$-SiLIPSS are shown in Figs. 4(a) and 4(b), respectively. The quadratic symbols in these figures represent the experimental data and solid line represents their linear fit lines. The reaction rate constants obtained from the slope of the linear fit line of these graphs are given in Table 2. As can be seen from this table, the reaction rate constants of sample $HPTiO_2$-NoLIPSS and $HPTiO_2$-SiLIPSS are 0.26 and 0.54 h^{-1}, respectively.

From the ratio of these reaction rate constants, the enhancement factor of photocatalytic dye decomposition activity of high pressure grown TiO_2 thin film in presence of LIPSS is found to be 2.1 (Table 2).

Similarly, the $\ln(C_0/C)$ versus time graph for low pressure grown TiO_2 thin films, $LPTiO_2$-NoLIPSS and $LPTiO_2$-SiLIPSS are shown in Figs. 5(a) and 5(b), respectively.

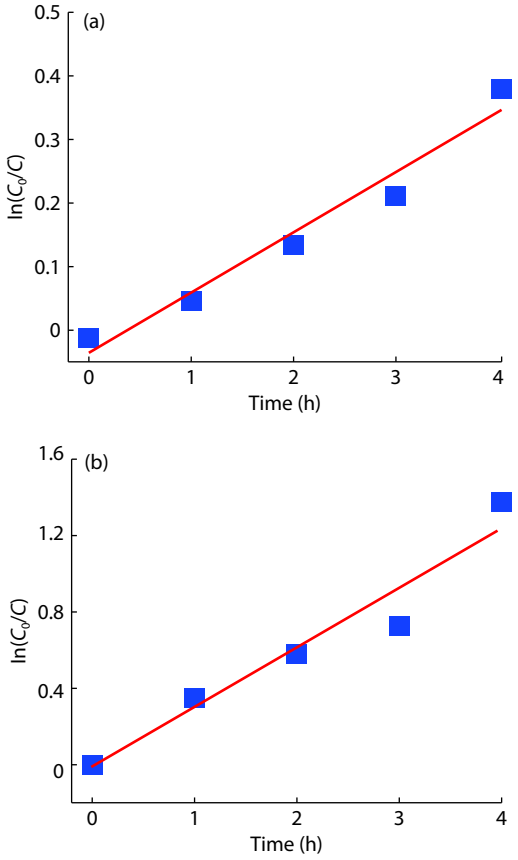

Fig. 5. (Color online) $\ln(C_0/C)$ versus photocatalysis time graph for low pressure grown TiO_2 thin film on Si substrate containing no LIPSS (LP-TiO_2-NoLIPSS) and LIPSS (LPTiO_2-SiLIPSS).

Table 3. Reaction rate constant of low pressure grown TiO_2 thin film on Si substrate containing no LIPSS (LPTiO_2-NoLIPSS) and LIPSS (LP-TiO_2-SiLIPSS).

Name of sample	k (h^{-1})	Enhancement factor
LPTiO_2-NoLIPSS	0.09	3.3
HPTiO_2-SiLIPSS	0.31	

The reaction rate constants obtained from the slope of the linear fit line of these graphs are given in Table 3.

As can be seen from this table, the reaction rate constants of sample LPTiO_2-NoLIPSS and HPTiO_2-SiLIPSS are 0.09 and 0.31 h^{-1}, respectively. From the ratio of these reaction rate constant the enhancement factor of photocatalytic dye decomposition activity of low pressure grown TiO_2 thin film in presence of LIPSS is found to be 3.3 (Table 3).

It is to note here that the enhancement factor in low pressure TiO_2 thin film is greater than high pressure TiO_2 thin film. The inferior photocatalytic property of LPTiO_2-NoLIPSS is probably the main cause for this.

3.5. Possible cause for enhancement of photocatalytic activity

The LIPSS generally increase roughness and surface area. This phenomenon has already been exploited in frame of applications like increase of friction, wettability etc.[4, 18]. Kuladeep *et al.*, have demonstrated that the SiLIPSS generated by fs laser can offer rms roughness as high as 50 nm[19]. In the present case, the similar increase of roughness was observed in AFM study of the LIPSS (Fig. 6). The cross-sectional

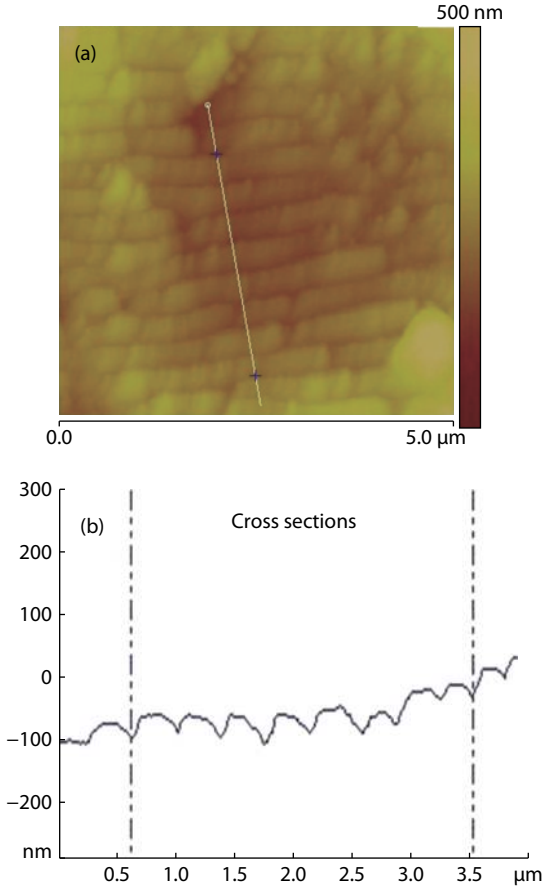

Fig. 6. (Color online) (a) AFM image of the LIPSS on Si (Inset: Selected line for cross-sectional analysis). (b) Cross-sectional analysis across the selected line of (a).

analysis (Fig. 6(b)) of AFM image (Fig. 6(a)) indicates that LIPSS contains the crests and valleys like structures. These crests and valleys increase the surface area of the deposited thin films. It can be assumed that this factor is responsible for an enhanced photocatalytic activity in our case.

3.6. Comparison of photocatalytic activity of the grown samples with standard reference material

For a reliable evaluation of the enhancement of photocatalytic behavior caused by the newly grown photocatalytic thin film, a comparison to a reference surface is required. One of the best established methods is the calibration with a standard reference thin film like Pilkington Activ™. The result of such a comparative study is shown in Fig. 7. The reference photocatalytic activity is estimated from the dye decomposition efficiency of various samples after 4 h of photocatalytic activity. As can be seen from this figure, the low pressure grown TiO_2 thin film on Si containing no LIPSS (LPTiO_2-NoLIPSS sample) shows much inferior photocatalytic activity than Pilkington Activ™ however when it is grown on LIPSS (LPTiO_2-SiLIPSS) it can show 1.25 times higher photocatalytic activity than this reference material. The high pressure grown TiO_2 thin film on Si containing no LIPSS (HPTiO_2-NoLIPSS sample) on the other hand shows almost similar photocatalytic activity as Pilkington Activ™ reference however when it is grown on LIPSS (HPTiO_2-SiLIPSS) it can reach about 1.5 times higher photocatalytic activity compared to the reference material.

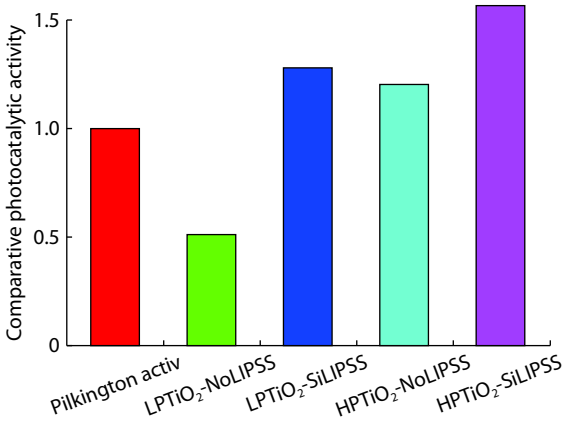

Fig. 7. (Color online) Comparative dye decomposition activity of various samples with respect to standard reference thin film Pilkington Activ™ after 4 h of photocatalysis.

3.7. Significance of present photocatalytic activity enhancement method with respect to the previously reported methods

It has to be noted that a number of methods like doping[20–26], selective-fluorination, etching processes[27], ion implantation[28], laser annealing[29], surface modifications[30, 31] etc. have been used for enhancing the photocatalytic activity of TiO_2 thin films. All these methods involve the co-material growth-step or after-material-growth steps to enhance the photocatalytic activity. Here, co-material growth-step means that the processing step is done with thin film during its growth and after-material-growth step means that the processing step is done with the thin film after the growth of material. Unlike these methods, the enhancement method reported in this work involves the pre-material growth-step on the substrate i.e. though this method the surface area of the substrate is increased prior to the deposition of the thin film. So, all the aforementioned methods can also be used in conjunction with the method reported in this work. Thereby our method can open a possibility of enhancement of photocatalytic activity by exploiting multiple mechanisms. Lastly it has to be noted that recently some pre-material growth-step on substrate like in situ polymerization[32], plasma surface modification[33], multi-heterojunction[34] have been demonstrated to enhance the photocatalytic activity of TiO_2 thin film. In terms of simplicity, reproducibility and controllability our method can be much better than the in situ polymerization and plasma surface modification whereas multi-heterojunction can be used in conjunction with our method thereby increasing the photocatalytic activity drastically.

4. Conclusions

To conclude, LIPSS on Si were generated by using a femtosecond laser. The typical period of the LIPSS was 500 nm and their orientation was found to appear perpendicular to the laser polarization. Photocatalytic substrates were prepared by depositing TiO_2 thin films on Si surface areas with and without LIPSS. For this purpose, sputtering from a Ti target into two types of oxygen atmospheres were applied. In the first case, the oxygen pressure in the sputtering chamber was chosen to be high (3×10^{-3} mbar) whereas it was by one order of magnitude lower in the second case (2.1×10^{-3} mbar). In the dye decomposition study with MB dye it was found that the presence of LIPSS leads to an enhancement in the photocatalytic reaction rate constant by 2.1 and 3.3 times for high pressure and low pressure grown TiO_2 thin films, respectively. The enhancement of surface area in presence of LIPSS is believed to be responsible for the enhanced photocatalytic activity in the present case. Moreover, in a comparative study it was found that the TiO_2 thin films grown on LIPSS under low and high oxygen pressure shows a 1.25 and 1.5 times higher photocatalytic activity than the standard reference sample Pilkington Activ™ .

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