APPLICATIONS OF SURFACE STRUCTURING WITH LASERS

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Abstract

Surface properties are significant in determining the applications of a material, and the modifications of surface properties have been drawing wide attention. The properties attracting the most attention include hydrophilicity, microhardness, optical properties, and tribological properties. To modify these surface characteristics, numerous methods have been developed and investigated over the years; however, they have limitations such as the involvement of toxic chemicals or the lack of spatial resolution. Free from these drawbacks, laser surface structuring is a promising method for surface property modifications. It provides high temporal and spatial resolution, noncontact processing and hence can maintain a high degree of purity. It also delivers a high quantum of energy to induce a very high heating and cooling rate, thermal gradient and resolidification rate. In this paper, laser surface structuring is reviewed in two fronts: the topography change, in which a desired surface topography is created, and the microstructure change, which alters the surface crystallinity and crystal structure. Simultaneous modification of topography and microstructure is also considered. Recent studies on the modifications of surface properties and applications caused by laser structuring are reviewed. Future perspectives are also presented.

Introduction

Surface Property Modifications and Applications

While a surface is generally defined as the outermost layer of a material, depending on the property being modified, the surface layer thickness of interest can range from several atomic layers to several crystal grains. Properties receiving wide attention include hydrophilicity, optical properties, and tribological properties. To modify these properties, various methods have been investigated. For hydrophilicity modification, chemical grafting [1] and plasma treatment [2] have been used. Methods involving chemical modifications or surface coatings have also been investigated to adjust optical [3] and tribological properties [4]. Use of chemicals is not acceptable in some medical applications due to toxicity, and the above-mentioned methods generally do not provide a high spatial resolution on the treated area. Laser treatment has been attracting increasing attention due to its high spatial resolution and non-contact processing and is emerging as a promising tool for surface property modifications.

Surface Property Modification by Laser Structuring

Laser surface structuring provides high temporal and spatial resolution, noncontact processing and hence a high degree of purity. It is also capable of delivering a high quantum of energy to induce a very high heating and cooling rate, thermal gradient and resolidification rate. Lasers with different wavelengths can be absorbed to different extents by a single material, and can also deliver photons with different energies. These characteristics cause lasers to be widely utilized for surface structuring procedures. There are two main aspects of laser surface structuring: topography change, in which a desired surface texture is created, and microstructure change, which alters the surface crystallinity and crystal structure. Laser structuring has been widely used to modify the properties mentioned above. Its capability to modify microstructures also allows for modification of thin film shape memory alloys (SMA) [5-7]. Recently, surface amorphization of biodegradable polymers used in drug delivery by laser irradiation [8] has been investigated with the aim to modify their degradation profiles [9,10]. Good reviews of tribological applications of laser texturing have been provided by [11]; the current paper will emphasize the applications enabled by laser-induced modifications of hydrophilicity, microhardness, and optical properties, as well as applications in SMA and biodegradable polymers.

Topography Modification

Laser treatment can induce topography modification of materials through various mechanisms. The most direct method is thermal ablation, while patterning through optical interference or hydrodynamics is also possible. The optimal texturing mechanism depends on the size scale of texturing that is required.

Patterning by Thermal Ablation

In thermal ablation processes, a high quantum of energy interacts with the irradiated material which is removed by vaporization. In such processes, micro-sized features are created on the surface and roughness is increased. A typical surface morphology after laser treatment is shown in Fig. 1 [12]. Each hole on the surface was formed through direct ablation by a number of laser pulses. By controlling pulse locations, a honeycombed structure is created where the surface roughness increases with the hole depth. The roughness is shown to vary with laser treatment parameters. By increasing laser fluence and pulse duration, the structures with deeper holes are formed on the textured surface. The feature size, however, is limited by the spot size of the incoming laser beam, which is at minimum on the order of microns.

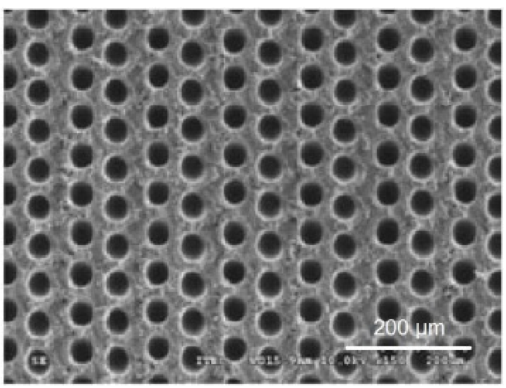

Fig. 1. SEM micrographs of a silicon surface treated by a Nd:YAG laser. Laser treatment induces surface roughness, which enhances the hydrophilicity of the surface [12].

The textured surface and increased roughness induced by this method have found a variety of applications in bio-related fields including medical implants and tissue engineering. In such applications, cell adhesion is of interest. Studies on the interaction between microstructured surfaces and cells have been performed on polymeric materials. The textured structures, in the form of grooves or holes, improve cell adhesion and help guide cell growth. This characteristic has been applied to enhance the interaction between artificial and biological systems in retina implants [13]. The device is developed for patients suffering from retina degeneration. These patients are able to see through electrical stimulation of the optical nerve. The stimulation electrodes are embedded into a biocompatible polymer, polydimethylsiloxane, which is perforated with laser radiation so that proliferating cells can fix the implant on the retina surface.

Cell adhesion is also affected by surface hydrophilicity; higher hydrophilicity favors cell adhesion. Hydrophilicity is defined as the interaction of solid, liquid and gas phases, and can be characterized by contact angle measurements. In the case of water, surfaces with contact angles between 0° and 90° are considered hydrophilic, between 90° and 180° are considered hydrophobic. Topography change by laser structuring has been shown to adjust surface hydrophilicity. Studies performed on the biocompatible polymer, polymethylmethacrilate (PMMA) [14] report that the contact angle decreases with the increase of irradiation pulses, suggesting increased hydrophilicity. Given the same number of laser pulses, higher fluence has been shown to lead to a more hydrophilic PMMA substrate.

On the other hand, hydrophobicity is also required in medical applications such as surgical tools. During gripping or cutting of human tissues, sticking phenomena often occur between the tissue and tool. This can be found in radiofrequency surgery, which uses a steel electrode to open human tissues while heat is produced to coagulate blood. The sticking phenomena can reopen the coagulation, requiring that the steel electrode be replaced. Increasing hydrophobicity of the tools is an effective way to solve the problem. Attempts have been made to increase the hydrophobicity of steel, and have shown that the contact angle increases with increasing groove depth. A contact angle up to 130° can be achieved by optimizing laser treatment parameters [15].

Improvements in hydrophilicity or hydrophobicity can often be achieved by increased surface roughness depending on the original hydrophilicity of the surface [12,14-16]. In particular, with increasing roughness, hydrophilic surfaces become more hydrophilic, and hydrophobic ones become more hydrophobic, as described by Wenzel's model [17]. If very rough, on the other hand, an originally hydrophilic surface can also become hydrophobic [15], as predicted by Cassie [18]. This theory assumes that the undulations of the rough surface trap air, and the liquid does not completely wet the roughened surface. This suggests that roughening a surface always increases the contact angle which is not always supported by experiments. Based on the two theories, whether hydrophilicity can be increased or decreased depends on the original hydrophilicity and roughness of the material, and requires factual experimental tests.

Patterning by Optical Interference

Surface texturing can also be created by the interference between the incident polarized laser light and the light scattered from the irradiated surface. The light is scattered due to surface impurities or defects, and the interference induces periodic energy density undulation on the surface. This generates wavelength-scale surface structures with directionality and periodicity, known as laser-induced periodic surface structure (LIPSS). This allows for formation of features in the nano-scale which is significantly smaller than achievable by direct ablation.

LIPSS is attracting increased interest because of its potential applications in MEMS systems. The ripples formed by LIPSS may be applied to fabricate gratings and shallow junctions, as well as to texture magnetic recording media. The ripple structure can also be used to roughen the surface of MEMS components to improve the performance or lift time of micro-devices by enhancing surface adhesion.

Since the polarized laser pulses have a directional electric field, polymer functional groups will align themselves along the electric field during LIPSS formation [19]. This uni-directional polymer alignment has been used in piezo-electricity, liquid crystalline molecular alignment, and strengthening of polymer films in addition to surface texturing.

LIPSS generally refers to low-spatial frequency LIPSS (LSFL) with wavelength-scale ripple structures, and has been observed to occur on most materials. Theoretical studies for LSFL have been proposed [20]. Recently, high-spatial frequency LIPSS (HSFL) with the spatial period less than the incident laser wavelength was produced on various solids mainly by femtosecond lasers. The origin of HSFL is still under discussion. One mechanism proposed is the interaction of incident laser light with laser-produced surface plasma [21,22]. Another mechanism involves the second harmonic generation generated on a rough surface structured by the LSFL, which is supported by an observation of transition from LSFL to HSFL, as given in Fig. 2 [23]. Figure 2(a1-c1) shows the SEM images of LIPSS on the surface of the laser treated superalloy CMSX-4. Figure 2(a2-c2) shows the gray value profiles along the trace path in Fig. 2(a1-c1), respectively. The SEM images and topography profiles clearly demonstrate the morphological evolution of LIPSS. First several pulses produce the periodic ripples of classical LSFL with the period approximately equal to the laser wavelength. As the pulse number increases, new grooves appeared and become more distinctive on the main ridges, and eventually form the HSFL.

Due to its ability to form nano-scale structures, HSFL is able to modify and enhance the optical absorption of a material. It has thus been used in the aesthetics applications in which a metal is colored without coating. One study has shown the ability to make an aluminum can appear gold, black, or gray [24]. The reflectance of the gold-colored aluminum drops over the entire measured wavelength range compared to the untreated aluminum. The drop is more pronounced as the wavelength decreases. This spectral dependence will induce a greater absorption at blue and green wavelength range, leading to a golden color. By adjusting laser treatment parameters such as the fluence, repetition rate, and scanning speed, the absorption characteristics of the material can be modified allowing for different colors to be achieved.

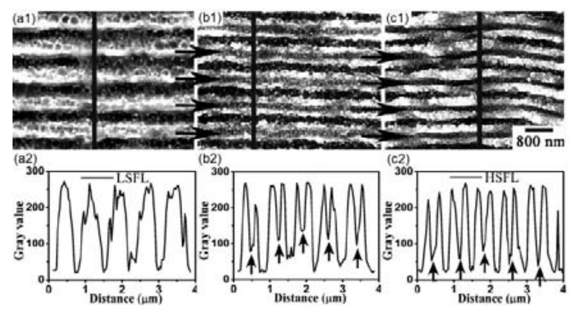

Fig. 2. SEM measurements and topography (represented by the gray value obtained in SEM images) of surface treated with increasing pulse number from left to right, demonstrating the process of HSFL generation [23].

Patterning by Surface Hydrodynamic Effects

Surface hydrodynamic effects can also lead to the formation of micro-scale spikes on a surface irradiated by a femtosecond or nanosecond laser. Due to the high density of the spikes and their sharp tips, such structures achieve highly efficient light trapping and absorb an appreciable fraction of light incident on the textured surface. They are thus primarily used for optical absorption enhancement. Since silicon has been widely used as the solar cell material, significant effort has been devoted to texturing the silicon surface with the aim to enhance light absorption. Such treated silicon surfaces demonstrate a higher absorbance over a wide range of wavelengths [25].

In addition to modifying optical properties, the spike structures have been shown to decrease hydrophilicity due to a reduced surface contact area between the textured surface and the liquid, as predicted by Cassie [18]. In an attempt by Schlie et al. [26], materials for orthopedic applications (silicon and titanium) were treated by a femtosecond laser, and the liquid interaction was changed from hydrophilic to hydrophobic. This has potential applications in selective cell control via proliferation [26].

There are two mechanisms to form the spike structures through hydrodynamic effects: ablation dominant formation, and growth dominant formation. They are generally achieved by femtosecond and nanosecond lasers, respectively. The processing environment has also been shown to have an effect on the resultant texture and light absorption capabilities.

Ablation Dominant Spike Formation Femtosecond laser irradiation has been shown to form micrometer-sized spikes on silicon surfaces after hundreds of pulses. [27-29]. The tips of the spikes are at or below the original surface height. This suggests that ablation is the dominant mechanism for spike formation [27]. The development of the spikes has been studied as a function of pulse number [28,30]. Ripple patterns are observed on the surface treated with two laser pulses. The ripple formation is believed to be in agreement with the LIPPS mechanism. As pulse number increases, the ripple pattern disappears and is replaced by small beads. When the pulse number increases to several hundred pulses, material is preferentially ablated on the sides of the beads, and the beads concentrate the light into the valleys between them leading to preferential ablation in the valleys for subsequent pulses. A representative image is given in Fig. 3 [30]. The rounded shape of spike tips may be due to redeposition of vaporized material on the tip.

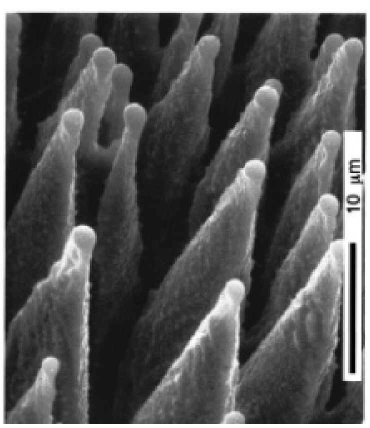

Fig. 3. The SEM image of a silicon surface after femtosecond laser treatment with 500 pulses [30].

Growth Dominant Spike Formation As opposed to the ablation-dominant spike formation caused by femtosecond lasers, silicon surfaces treated by a nanosecond laser can form spike tips higher than the original surface [28,31], which suggests a growth mechanism of spike development. Figure 4 shows micro-columns on a silicon surface grown by nanosecond laser irradiation [31]. The spike height increases with pulse number. The melted depth (around 2 μm) is much less than the spike height. The solid pedestal separates the melted material produced at the tip from that produced on the substrate during irradiation. Also, the sides of the columns are almost vertical, and they do not melt because incident laser energy on them is negligible. It is believed that, during the spike formation, silicon-rich vapors are produced in the grooves or holes formed during the first few pulses where ablation is enhanced because of the highly-concentrated laser energy. The vapor is then transported to the tip of the spike through redeposition [31].

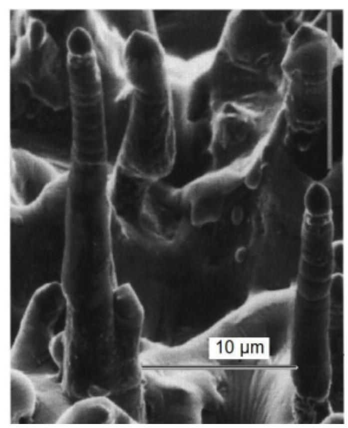

Fig. 4. SEM image of a silicon surface treated by a nanosecond laser [31].

The spike morphology generated with femtosecond and nanosecond laser pulses show significant differences. The former are covered with a disordered nanocrystalline surface layer, while the latter have very few nanocrystals on the surface. Despite the difference, both types exhibit remarkable light absorption performance: near-unity, uniform absorptance from 0.4 to 1 μm, a small decrease in absorptance around 1.1 μm, and strong uniform absorptance from 1.1 to 2.5 mm [25].

Processing Medium Effect on Spike Formation The effects of processing medium during laser treatment have also been studied, and the processing medium has been found to significantly influence the spike morphology obtained [29,32]. Figure 5 shows the silicon surface morphology treated by femtosecond laser in SF_6, Cl_2, N_2, and air [29]. It is found that treating in SF_6 or Cl_2 leads to sharp conical structures with tip radii of approximately 500 nm. Moreover, the structures made in SF_6 have a greater degree of surface roughness when compared to the Cl_2-prepared structures. On the other hand, structures obtained in air or N_2 are much more rounded than those made in halogen-containing gases. Additionally, treating in air induces significant surface roughness on the spikes themselves; this roughness appears less dendritic than the formations on the SF_6-prepared spikes. The number density of conical structures also depends on the ambient gas, with higher densities achieved in halogen-containing gases. Surfaces prepared with SF_6 yield the greatest number density, followed by Cl_2. The differences in morphology stem from different chemical species created in the gases. It is well known that halogens create volatile compounds with silicon whereas other gases do not which is believed to be the cause of the sharper spike shape.

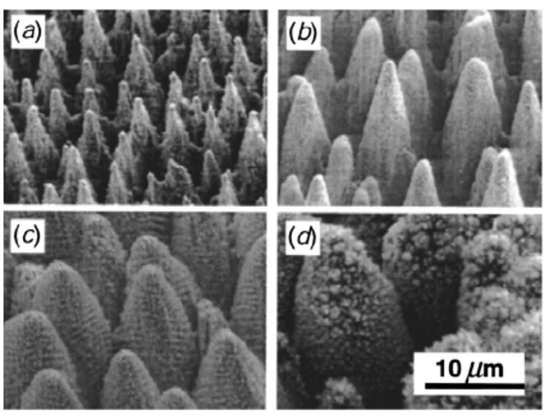

Fig. 5. SEM images of the conical silicon microstructures formed by femtosecond laser irradiation in a background gas of (a) SF_6, (b) Cl_2, (c) N_2, and (d) air [29].

The light absorbance of the structures treated in different media has been studied by Younkin et al. [29]. All samples show an increase in infrared absorption, while the effect is strongest for structures formed in SF_6, followed by those treated in Cl_2. Surfaces structured in air or N_2 are less effective absorbers than those treated in halogen-containing gases. The high absorbance of the structures formed in SF_6 stems from the sulfur impurities either in the cones or in the rough features on the walls of the cones.

Microstructure Modification

Due to the high heating and cooling rate induced by laser irradiation, surface microstructure and crystallinity can be modified, and new phases can also be created. The optimal processing mechanism depends on the crystallization kinetics of the material and the desired microstructure.

Amorphization

Due to their slow crystallization kinetics, polymers melted by pulsed lasers do not crystallize during the cooling process, causing surface amorphization. Such treatment has recently been applied to biodegradable polymers used for drug delivery [9,10]. In such applications, drugs are embedded in a polymer matrix and are released as it degrades. However, due to the induction period of polymer degradation, the designed release rate cannot be achieved directly after drug implantation. A way to modify the degradation rate of biodegradable polymers is to change their crystallinity. It is proposed that PLA degradation begins in the amorphous region between lamellae, followed by the disorientation of the lamellae and disappearance of the spherulitic structure, and less crystalline regions degrade faster [33]. Therefore, decreasing surface crystallinity may accelerate the initial degradation rate. Using a Nd:YAG laser, surface crystallinity of biodegradable polymers have been reduced, and molecular conformations have been studied [9]. Rapid melting at the surface quench is numerically determined to be on the order of 10^6 K/s, which prohibits recrystallization during cooling. Excimer lasers have also been utilized to achieve uniform surface treatment [10]. The degree of crystallinity and chemical modifications due to laser treatment are studied, and the effect of free radical mobility on the amount of chemical modifications is considered. The

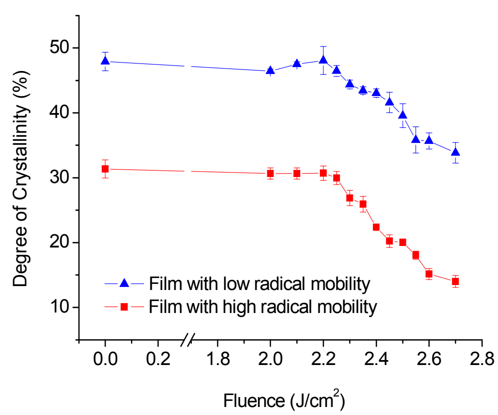

Fig. 6. Crystallinity of PLLA films derived from the WAXD results as a function of laser fluence [10].

chemical modifications come from excimer irradiation, since it generates photons with energy higher than certain polymeric bond energy. Annealed films have low radical mobility, and non-annealed films have high radical mobility. The degree of crystallinity as a function of laser fluence is shown in Fig. 6, which shows that crystallinity decreases for fluences above a certain threshold. This threshold is thought to represent the fluence at which polymer melting occurs. This figure also shows that the crystallinities of both films decrease at the same fluence. On the other hand, the film with low radical mobility requires a larger fluence to induce appreciable chemical changes. Such films thus have a better applicability of excimer laser surface treatment. Regarding surface morphology, laser treatment can induce bubbles on the surface, which suggests chemical decomposition; however, this can be reduced via decreasing fluence and/or radical mobility.

Crystallization and Formation of Novel Phases

Laser irradiation allows new crystals and phases to form on the treated surface. These newly formed crystals and phases can modify surface microhardness and hydrophilicity, depending on the material and microstructures formed.

Microhardness Because of their low densities and high specific strengths, some metals and alloys, such as aluminum and magnesium, have a wide scope of applications in the aerospace and automotive industries where weight reduction is a concern. Despite their advantages, they generally suffer from a relatively poor wear resistance. Surface microstructure modification by laser treatment has been found to be a potential way to increase the microhardness. In this process, novel phases and microstructures can be formed in the laser processed zone owing to the rapid heating and cooling rates. These changes in phase components and surface microstructure can result in increased surface microhardness. Yang et al. have shown that, for aluminum alloys [34], higher levels of hardness can be achieved when the formation of the intermetallic phase, nickel aluminide, is increased. The microhardness and corrosion resistance of ZE41 Mg-alloy has also been enhanced by laser processing. This enhancement is thought to be due to the characteristic that the melted Mg-alloy forms a homogenous distribution of the alloying elements [35].

Hydrophilocity In addition to surface texturing discussed before, hydrophilicity modifications can also be induced through microstructural changes in alloys, metal-based oxides, and ceramics. Hydrophilicity modification of bioceramics can be applied to tissue engineering applications, while hydrophilicity modification of metallic materials can be used to enhance coating adhesion for greater durability or for corrosion resistance. Cooling rates induced by laser irradiation can allow crystallization, and increased hydrophilicity has been observed on the newly formed microstructure [36,37]. In studies conducted by [36], a CO_2 laser is used to treat magnesia partially stabilized zirconia (MgO-PSZ), where the laser irradiation results in rapid heating of the surface and consequently leads to the crystal growth in the melted layer. The newly formed microstructure is comprised of larger crystals that likely improved the action of wetting and adhesion by increasing surface energy.

Thin Film Shape Memory Alloys Thin film shape memory alloys are a promising material for use in micro-scale devices. NiTi is one of the most popular biomaterials in use today, and for the past two decades, it has been used in various medical applications, such as minimal invasive surgeries, diagnostic applications, as well as orthodontic appliances [38]. The effect of laser surface processing on the microstructure of NiTi has been attracting significant attention recently [5-7] with efforts being directed toward adjusting the microstructure of the NiTi films in order to modify their shape memory properties. Investigations of laser processing temperature on crystallization of NiTi thin films have been conducted [5]. It is determined that processing at elevated substrate temperatures would significantly reduce the quench rate, and thus have added potential for resulting in the desired

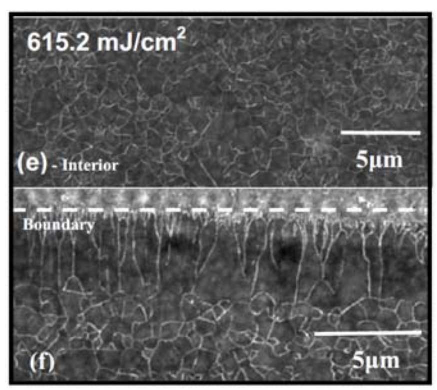

Fig. 7. Representative image from completely melted film treated at the elevated temperature (800 °C). Completely melted film is characterized by the presence of large aspect ratio, well defined lateral growth [5].

microstructure, phase, mechanical, and shape memory responses. When processed at 600°C or above, the well defined lateral growth occurs at the boundary, as given in Fig. 7, and is a direct evidence of film having undergone complete melting and growth of desired phase [5].

To tailor the shape memory response, the martensitic phase transformation temperature can also be controlled through laser treatment. High laser fluences have been shown to decrease transformation temperatures [5]. This can be explained by the fact that increases in laser fluence enhance melting depth, which results in decreases in film stress giving rise to the change in material response. The orientation of the anisotropic NiTi crystals in a NiTi thin film have also been modified using a pulsed laser melting process. To investigate the phases of the films after laser crystallization, the electron backscatter diffraction (EBSD) measurements have been conducted [7]. Figure 8 shows a representative EBSD map of a processed film with Euler angle coloring covering an area of 100μm by 50μm. Figure 8b is an inverse pole figure for the surface normal orientation which shows evidence of a (110) preferred orientation in the sample. The (110) orientation has the lowest surface energy in BCC materials which can causes preferential growth of (110) oriented grains as the film solidifies and results in an increase in the area fraction of those grains. The creation of crystal texture allows for a strong anisotropic shape memory response even in polycrystalline thin films.

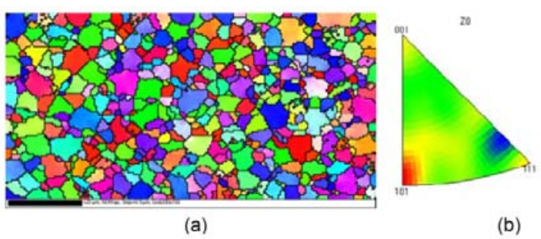

Fig. 8. (a) Representative EBSD map for normal direction of laser crystallized film with Euler angle coloring. Inverse pole figure (b) showing slight (110) texture normal to the film surface [7].

Simultaneous Topography and Microstructure Modification

Hydrogenated amorphous silicon (a-Si:H) thin films have been considered for use in solar cell applications because of their significantly reduced cost compared to crystalline bulk silicon. Surface texturing, as discussed before, increases light trapping and thus light absorbance. However, texturing alone does not solve the stability issues faced by a-Si:H. The low stability is a result of the light-induced degradation known as the Staebler-Wronski effect (SWE) [39]. Efforts have been made to solve each problem separately. To increase the efficiency of silicon solar cells, antireflection coatings and front-side texturing have been used to enhance light trapping. To combat the problem of the SWE, crystallization of a-Si:H is a solution, and ultrafast laser treatment is a new approach for inducing crystallization in this material [40,41]. Due to the interaction between the laser irradiation and the material during crystallization processes, surface texturing is also induced. The created texture enhances light trapping and thus absorption. Accordingly, the ultrashort laser treatment serves as the one-step process, simultaneously producing surface structuring and crystallization [40,41].

The effects of laser processing parameters and processing medium on crystallization have been investigated [41] and have shown that samples treated in air have higher crystallinity than those treated in water. This is due to a higher cooling rate in water than in air, and the melted silicon resolidifies so quickly that much material is unable to crystallize. Samples treated with lower fluences and higher scanning speeds have shown higher crystallinity. Similarly, this is attributed to the reduced cooling rate caused by the lower surface temperature and temperature gradient. The resulting absorptance spectra indicate that the samples treated in air have the best absorption performance over the solar radiation spectrum. The conical spikes and attached nano-particles formed on the sample treated in air can induce greater light reflection and scattering between the spikes. The greater crystallinity formed during the laser processing in air also leads to a wider absorption spectrum since crystalline silicon has a different band gap than amorphous silicon. These effects all work to increase the absorptance of the sample treated in air.

The effect of hydrogen on surface texturing and crystallization of a-Si:H thin film is also a topic drawing increasing attention recently. Figure 9 shows the cross-sectional TEM images of an a-Si:H thin film treated by a nanosecond excimer laser with 50 pulses [41]. It can be seen that the microstructure can be divided into two regions: the large- and fine-grained regions. Front-side transient reflectance (FTR) measurements (not shown) suggest that explosive crystallization occurs within 20ns of the start of the laser pulse which forms the fine-grained region, and after that, the top layer is melted again because of the heat accumulation caused by the rest of the pulse. The hydrogen atoms inside the material start moving by absorbing the laser energy and aggregating at the interface between the solid and liquid silicon. Those hydrogen atoms combine as molecules and form bubbles, and those bubbles keep dilating and explode when the internal pressure inside the bubbles becomes higher than the outside. The bubble explosion at the liquid/solid silicon interface drives the liquid silicon upward and the surrounding liquid flows towards it. During the process, the liquid silicon is not stable. Before the liquid silicon become stable, the material solidifies and forms spikes with a height of ~350nm and large bubbles are left at the interface. Because the molten layer at the surface can last for almost 20ns, the crystallized material can form much larger grains (~140nm) than that formed during explosive crystallization.

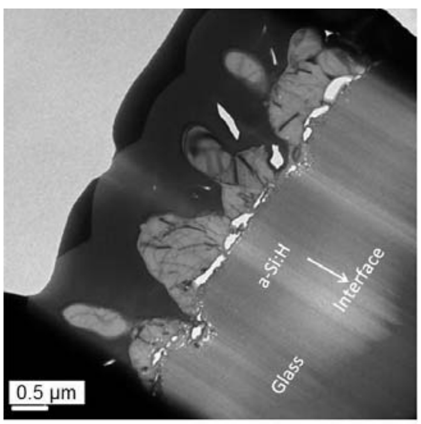

Fig. 9. Cross-section view TEM micrographs of the a-Si:H sample irradiated by nanosecond laser pulses [32].

Future Perspectives and Conclusions

This paper has reviewed the modifications of hydrophilicity, microhardness, and optical properties through laser surface structuring. Applications allowed by these modified properties, as well as applications in SMA and biodegradable polymers have also been emphasized. Recent research efforts indicate that laser structuring has found increasing applications in bio-related areas. The features generated by laser structuring have also reduced from micro-scale to nano-scale.

Modifications of hydrophilicity and hydrophobicity caused by laser surface structuring have been undergoing continued development for nearly two decades, and have found applications in metallization of non-metallic materials as well as adhesion in the microelectronic or microsystem technologies. More recently, these same types of modifications have found applications in tissue engineering and medical implant technology. The hydrophilicity and hydrophobicity of the surface of biomaterials such as biocompatible polymers and titanium alloys have been modified to enhance properties such as cell adhesion and proliferation. The high spatial resolution and precise heat input of laser texturing processes has enabled more and more complex surface structures to be formed which has further expanded the capabilities available to researchers in this field.

While past laser texturing processes have been limited in length scale to the wavelength-level texturing offered by optical interference and hydrodynamic texturing mechanisms, the recently developed HSFL process has enabled sub-wavelength texture to be formed. In addition to silicon, HSFL has also been found in a variety of materials including metals, glass, and polymers. HSFL has been used to modify the color of aluminium surfaces and is expected to produce new, novel applications in the optical and medical fields. Mechanisms of HSFL formation, however, are not well understood. Further experimental and numerical investigations are required for a better understanding of this phenomenon, as well as for a better control of the features induced.

With the capability to alter surface topography and microstructure, laser surface structuring provides a promising means to modify surface properties and enhance material performance in various applications. Based on the modifications of these properties, versatile applications have been discovered and developed. An emerging trend has also seen a shift to the applications in medicine or other bio-related fields, including SMA, drug delivery, and tissue engineering. It is envisioned that with further investigation in fundamental science and engineering, many more applications can benefit from laser structuring in the coming years.

References

[1] Park, S., Bearinger, J.P., Lautenschlager, E.P., Castner, D.G. & Healy, K.E. (2000) Surface modification of poly(ethylene terephthalate) angioplasty balloons with a hydrophilic poly(acrylamide-co-ethylene glycol) interpenetrating polymer network coating, J Biomed Mater Res 53(5), 568-576.

[2] Steen, M.L., Hymasa, L., Havey, E.D., Capps, N.E., Castner, D.G. & Fisher, E.R. (2001) Low temperature plasma treatment of asymmetric polysulfone membranes for permanent hydrophilic surface modification, J Membr Sci 188, 97-114.

[3] Frank, W.F. (1998) Surface modification of polymers by ionizing radiation: optical and mechanical effects, SPIE Conf Mater Modif Ion Irrad 3413.

[4] Wu, F.B., Li, J.J. & Duh, J.G. (2000) Evaluation of the mechanical properties and tribological behavior of the CrN coating deposited on mild steel modified with electroless Ni interlayer, Thin Solid Films 377-378, 354-359.

[5] Birnbaum, A.J., Chung, U.J., Huang, X., Im, J.S., Ramirez, A.G. & Yao, Y.L. (2009) Substrate temperature effects on laser crystallized NiTi thin films, Appl Phys 105, 073502.

[6] Birnbaum, A.J., Yao, Y.L., Chung, U.J., Im, J.S., Huang, X. & Ramirez, A.G. (2009) On the lateral crystal growth of laser irradiated NiTi thin films, Appl Phys Lett 94, 261908.

[7] Satoh, G., Yao, Y.L., Huang, X. & Ramirez, A. (2010) Characterization and prediction of texture in laser annealed NiTi shape memory thin films, Proc ASME 2010 Int Manuf Sci Eng Conf, MSEC2010-34250.

[8] Lazare, S. & Benet, P. (1993) Surface amorphization of Mylar films with the excimer laser radiation above and below ablation threshold: ellipsometric measurements, J Appl Phys 74(8), 4953-4957.

[9] Bhatla, A. & Yao, Y.L. (2009) Effect of laser surface modification on the crystallinity of poly(L-lactic acid), J Manuf Sci Eng 131, 051004.

[10] Hsu, S.-T., Tan, H. & Yao, Y.L. (2011) Effect of excimer laser irradiation of biodegradable polymer on its chemical bonding, ICALEO 2011 Congress Proc.

[11] Etsion, I. (2005) State of the Art in Laser Surface Texturing, J Tribol 127, 248-253.

[12] Tseng, S.F., Hsiao, W.T., Chen, M.F., Huang, K.C., Hsiao, S.Y., Lin, Y.S. & Chou, C.P. (2010) Surface wettability of silicon substrates enhanced by laser ablation, Appl Phys A 101, 303-308.

[13] Bremus-Kobberling, E. & Gillner, A. (2003) Laser structuring and modification of surfaces for chemical and medical micro components, Proceedings of SPIE Vol. 5063, 217-222.

[14] Qi, H., Chen, T., Yao, L. & Zuo, T. (2008) Hydrophilicity modification of poly(methyl methacrylate) by excimer laser ablation and irradiation, Microfluid Nanofluid 5, 139-143.

[15] Luo, B.H., Shum, P.W., Zhou, Z.F. & Li, K.Y. (2010) Preparation of hydrophobic surface on steel by patterning using laser ablation process, Surf Coat Technol 204, 1180-1185.

[16] Gachot, C., Hans, M., Catrin, R., Schmid, U. & Mucklich, F. (2009) Tuned wettability of material surfaces for tribological applications in miniaturized systems by laser interference metallurgy, Proc. SPIE Vol. 7362, 73620U.

[17] Wenzel, R.N. (1949) Surface roughness and contact angle, J Phys Chem 53(9), 1466-1467.

[18] Cassie, A. B. D. (1948) Contact angles, Discuss Faraday Soc 3, 11-16.

[19] Wong, W.Y.Y., Wong, T.M. & Hiraoka, H. (1997) Polymer segmental alignment in polarized pulsed laser-induced periodic surface structures, Appl Phys A 65, 519-523.

[20] Sipe, J.E., Young, J.F., Preston, J.S. & van Driel, H.M. (1983) Laser-induced periodic surface structure. I. Theory, Phys Rev B 27(2), 1141-1154.

[21] Sakabe, S., Hashida, M., Tokita, S., Namba, S. & Okamuro, K. (2009) Mechanism for self-formation of periodic grating structures on a metal surface by a femtosecond laser pulse, Phys Rev B 79, 033409.

[22] Miyaji, G. & Miyazaki, K. (2008) Origin of periodicity in nanostructuring on thin film surfaces ablated with femtosecond laser pulses, Opt Express 16(20), 16265-16271.

[23] Zhang, W., Cheng, G., Feng, Q., Cao, L., Wang, F. & Hui, R. (2011) Abrupt transition from wavelength structure to subwavelength structure in a single-crystal superalloy induced by femtosecond laser, Appl Surf Sci 257, 4321-4324

[24] Vorobyev, A.Y. & Guo, C. (2008) Colorizing metals with femtosecond laser pulses, Appl Phys Lett 92, 041914.

[25] Crouch, C.H., Carey, J.E., Warrender, J.M., Mazur, E. & Genin, F.Y. (2004) Comparison of structure and properties of femtosecond and nanosecond laser-structured silicon, Appl Phys Lett 84(11), 1850-1852.

[26] Schlie, S., Fadeeva, E., Koroleva, A., Ovsianikov, A., Koch, J., Ngezahayo, A. & Chichkov, B.N. (2011) Laser-based nanoengineering of surface topographies for biomedical applications, Photonics Nanostruct-Fundam Appl 9, 159-162.

[27] Her, T.H., Finlay, R.J., Wu, C. & Mazur, E. (2000) Femtosecond laser-induced formation of spikes on silicon, Appl Phys A 70, 383-385.

[28] Tull, B.R., Carey, J.E., Mazur, E., McDonald, J.P. & Yalisove, S.M. (2006) Silicon surface morphologies after femtosecond laser irradiation, MRS Bulletin 31, 626-633.

[29] Younkin, R., Carey, J.E., Mazur, E., Levinson, J.A. & Friend, C.M. (2003) Infrared absorption by conical silicon microstructures made in a variety of background gases using femtosecond-laser pulses,

Appl Phys 93(5), 2626-2629.

[30] Her, T.-H, Finlay, R. J., Wu, C., Deliwala, S. & Mazur, E. (1998) Microstructuring of silicon with femtosecond laser pulses, Appl Phys Lett 73(12), 1673-1675.

[31] Pedraza, A.J., Fowlkes, J.D. & Lowndes, D.H. (1999) Silicon microcolumn arrays grown by nanosecond pulsed-excimer laser irradiation, Appl Phys Lett 74(16), 2322-2324.

[32] Wang, H., Lusquinos, F. & Yao, Y.L. (2011) Effect of hydrogen on surface texturing and crystallization on A-Si:H thin film irradiated by excimer laser, J Manuf Sci Eng, submitted.

[33] Tsuji, H. & Ikada, Y. (1998) Properties and morphology of poly(L-lactide). II. hydrolysis in alkaline solution, J Polym Sci A Polym Chem 36, 59-66.

[34] Yang, Y & Hu, J. D. (2011) Effects of laser power density on the microstructure and microhardness of Ni-Al alloyed layer by pulsed laser irradiation, Optics Laser Technol 43, 138-142.

[35] Khalfaoui, W., Valerio, E, Masse, J. E. & Autric, M. (2010) Excimer laser treatment of ZE41 magnesium alloy for corrosion resistance and microhardness improvement, Optics Lasers Eng 48, 926-931.

[36] Hao, L., Lawrence, J. (2004) CO_2 laser induced microstructure features in magnesia partially stablised zirconia bioceramic and effects thereof on the wettability characteristics, Mater Sci Eng A364, 171-181.

[37] Guan, Y.C., Zhou, W. & Zheng, H.Y. (2009) Effect of Nd:YAG laser melting on surface energy of AZ91D Mg alloy, Surf Rev Lett 16(6), 801-806.

[38] Li, Q., Zeng, Y. & Tang, X. (2010) The applications and research progresses of nickel-titanium shape memory alloy in reconstructive surgery, Australas Phys Eng Sci Med 33, 129-136.

[39] Staebler, D.L. & Wronski, C.R. (1977) Reversible conductivity changes in discharge-produced amorphous Si, Appl Phys Lett 31(4), 292-294.

[40] Wang, X.C., Zheng, H.Y., Tan, C.W., Wang, F., Yu, H.Y. & Pey, K.L. (2010) Femtosecond laser induced surface nanostructuring and simultaneous crystallization of amorphous thin silicon film, Opt Express 18(18), 19379-19385.

[41] Wang, H., Kongsuwan, P., Satoh, G. & Yao, Y. L. (2011) Effect of processing medium and condition on absorption enhancement of femtosecond laser treated a-Si:H thin film, in Proceedings of NAMRI/SME 39.

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