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High-energy density beams and plasmas for micro- and nano-texturing of surfaces by rapid melting and solidification

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Abstract
Several advances in materials research have been made due to the wide array of tools currently available for the processing of materials: plasmas, electron beams, ion beams and lasers. The area of material science is fortunate to have seen the development of these tools over the years, be it for new bulk materials, coatings or for surface modification. Several applications have benefitted and many more will in the future as the properties of the materials are altered on a micro/nanoscale. Currently, several techniques exist to modify the physical, chemical and biological properties of the material surface; however, this review limits itself to surface modification applications using the rapid thermal processing (RTP) technique. First, a brief overview of the existing surface modification methods using the principles of RTP is reviewed, and then a novel method to create micro/nanostructures on the surface using pulsed plasma exposure of materials is presented.

1. Introduction
Materials research has been motivated to obtain better material properties than the existing materials. Research in nanomaterials is no exception—the grain size of these materials being in the nanoscale has given rise to superior properties compared with the conventional materials. A summary of changes in material properties due to the extremely small grain sizes in nanostructured materials is very well detailed by Suryanarayana [1] and references therein. These include increased strength/hardness, enhanced diffusivity, improved ductility/toughness, reduced density, reduced elastic modulus, higher electrical resistivity, increased specific heat, higher coefficient of thermal expansion, lower thermal conductivity and superior soft magnetic properties [1]. While nanomaterials have shown tremendous opportunity, synthesizing them with reproducible properties has remained an active engineering problem.

The development of new techniques for producing nanostructures is important for several engineering applications. The nanostructured materials could be synthesized either by the ‘top-down’ processing approach where the bulk material is modified to produce nanostructures on the surface, or the ‘bottom-up approach’ in which nanostructures are assembled from building blocks such as atoms, ions or molecules. Processing techniques such as sputtering, laser ablation and deposition schemes fall under the bottom-up approach. Top-down processing includes techniques such as rapid surface melting, rapid solidification processing (RSP), surface nanostructuring, etc. A very good review of papers producing nanocrystalline materials is already provided in a number of references [2–9] and this review will not cover those methods. Also, techniques involving severe plastic deformation methods have been successfully used in the formation of nanocrystalline surface layers in various metallic materials, as demonstrated in Satoa et al and references therein [10]. There is an abundant amount of research in nanomaterials that is available in the literature and it is beyond the scope of this review to cover all of them. Instead, what this review includes is the methods used to produce nanostructures based on rapid thermal processing (RTP) techniques.

The RTP of materials has been widely used in the microelectronics industry in the past for annealing of wafers and improving their properties [11].
of temperature is achieved in the RTP technique, which permits high heating and cooling rates that cannot be reached with conventional treatments. In recent years, RTP has been increasingly applied to the processing of materials for different applications. The controllable heating profiles allow structuring of material surfaces via expediting phase transitions and tailoring materials morphology.

Recently, the rapid rise of research and development in plasmas and lasers has seen the use of these tools for RTP. Electron beams, ion beams, lasers and plasmas have all been successfully used in the past for improving material properties and a review is provided in section 2. In addition, a novel pulsed plasma source which was originally developed for its use in extreme ultraviolet (EUV) lithography is used to tailor the surface properties in the micro/nanoscale, and the results are presented in section 3. Finally, a summary is provided in section 4.

2. The RTP technique

RTP is usually understood to be a semiconductor processing method, as this process dates back to the late 1960s [12], when IBM pioneered making submicrometre features using pulsed laser irradiation [13]. RTP is a tool that enables rapid thermal cycles which cannot be performed with conventional batch furnaces. The conventional furnace processing places a limitation on the maximum heating and cooling rates to few hundreds of K min⁻¹ and the processing time to several minutes. These restrictions are imposed by the high thermal mass of the system as well as the way the energy is transferred to the wafers. RTP, owing to its low thermal mass, enables high temperature gradients and faster processing times.

While RTP was dominated by laser processing in the early years, the later years saw a rapid rise in the use of other heating sources. A good review of heating sources for RTP systems is covered in [12]. Any process that involves fast heating and cooling rates could be placed in this category. Review papers [14–16] described the advantages of isothermal heating (lamp, resistance, and e-beam heating, 1–100 s processing time) over thermal flux (scanned continuous wave (cw) laser, e-beam, 0.1–10 ms processing time) and adiabatic heating (pulsed beam or laser, 1–1000 ns processing time) to semiconductor manufacturing [17,18]. However, the demands of RTP systems for material modification are quite different from those used in microelectronics applications. For material processing, the RTP technique involves rapid melting of the surface of a material followed by rapid quenching due to heat conduction into the unaffected bulk material. These require higher heating and cooling rates and so adiabatic heating presents an ideal RTP method for micro/nanostructuring of surfaces.

Increasing applications of RTP processing in materials processing, especially for producing micro- or nanostructures, has been seen in recent years. A good review of the RTP technique for its application in magnetic materials is covered in [19]. Several reviews relating to this subject are also available in the name of RSP, given by Suryanarayana [18], Jacobson [20] and references therein. The tools that are available to meet the needs of material modification are lasers, e-beams, ion beams and pulsed plasmas, and therefore these are covered in detail in this review.

2.1. RTP processing using electron beams

The use of electron beams over the years has increased tremendously and is now a commercial technology for several applications. For example, electron beams are increasingly used in manufacturing applications such as drilling, melting, welding, etc. In addition, electron beams, due to the wide range of possible energies, have also been used in material processing applications that include electron-beam processing, electron-beam texturing and sterilization applications. Recently, there has been an increased growth of their use in semiconductor manufacturing, as well as in deposition and lithography applications. In the view of nano-material processing, e-beams have been used in nanostructuring of materials using e-beam lithography [21] and also using e-beam deposition [22]. However, in this review, because the variants of RTP are being surveyed, we limit ourselves to the use of electron beams for material processing where the intense energy of the e-beam is deposited into a thin layer of bulk material in a short time, such that the structure of the surface is altered. It is possible to develop unique phases, and surface compositions through the appropriate combination of e-beam processing parameters. This results in the formation of either micro- or nanostructures that will significantly enhance the properties of the surface.

The structuring of material surfaces by the use of e-beams has been reported in the literature with different names, for example as the rapid quenching process, electron-beam surface melting process, electron-beam hardening process, etc. These surface structures are expected to improve properties such as hardness, wear, erosion and corrosion resistance.

Electron-beam rapid quenching involves the rapid interaction of material with an electron beam yielding a thin melt layer on the surface. During this rapid surface melting process, a certain amount of thermal energy is conducted to the bulk giving rise to a steep temperature gradient between the solid (bulk) and the liquid (melt). This gradient results in rapid solidification. The quench rate is mainly dependent on process parameters such as the beam power, traverse speed and the interaction time. As a result of high cooling rates, interesting metallurgical structures are produced on the surface. Mawella and Honeycombe [23] investigated the properties of an ultra-high-strength alloy steel after e-beam treatment and showed that the rapid quenching process leads to a high degree of grain refinement and an increase in solid solubility which, in turn, increases the amount of retained austenite. The lowering of martensite transformation temperature due to the high cooling rate and the increased solid solubility favour the formation of twinned martensite. The considerable increase in the microhardness of the rapidly quenched layer, with respect to that of the solid state quenched steel, is attributed to interlinked phenomena such as austenite grain refinement, the increased solubility and the martensitic structure [23].

In the electron-beam surface melting process, a surface layer is fused by means of an electron beam and resolidified quickly. The rapid solidification yields improvement in the
microstructure and increases the hardness of the remelted layers. Petrov [24] reported changes in the structural morphology of aluminium alloys in the electron-beam treated zones and also an increase in hardness as a result of surface doping. Markov et al [25] demonstrated the hardening and tempering zones in quenched U7A steel irradiated with a pulsed electron beam.

In the electron-beam hardening process, the heat generated by the e-beam impingement on the surface is used to transform the material phase, which is due to rapid conduction of heat into the relatively cold bulk interior of the material. Dimitrov et al [26] studied the electron-beam treatment of ion nitriding steel and found that the hardness increased. The high hardness is attributed to the refined structure consisting of a-solid solution (nitrous martensite) and y-solid solution (nitrous austenite) and dispersed fine nitride precipitations. They also reported an increase in wear resistance of the electron-beam treated layer, which is twice that of the ion nitried specimen. Song et al [27, 28] investigated the effects of electron-beam surface treatment on the microstructure and hardness of AISI D3 tool steel and showed that the microstructure of the hardened layer consisted of martensite, a dispersion of fine carbides and retained austenite, while the transition area mainly consisted of tempered sorbite. Also, the microhardness of the hardened layer on the surface increased dramatically with that of base material. The e-beam method has successfully been applied to the treatment of alloys as well. For example, Nagae et al [29] demonstrated the improvement in surface roughness and hardness of a Co–Cr–Mo alloy.

In the following years, several researchers reported the formation of new structures resulting in the improvement of several material properties under the same surface treatment method. In all these methods, pulsed electron beams are used to modify materials by depositing energy in them. To effectively change the surface of a material, the main requirement is that the beam energy must be dissipated adiabatically in a thin layer of bulk material in a short time. A pulsed electron beam capable of melting the surface layer of any material into depths of a few tens of µm at a rate of $10^6$–$10^9$ K s$^{-1}$ is used to achieve the desired structural conditions. The structures produced in this process are very fine grained down to nanometre size and sometimes exist in metastable phases. It is preferable to heat the treated layer without marked evaporation and boiling of the melted phase, and also without significant energy loss due to thermal conductivity inside the bulk material, which is the adiabatic mode of RTP.

The pulsed electron-beam facilities GESA I and GESA II were developed in cooperation between the Efremov Institute St Petersburg, Russia, and the Research Center Karlsruhe (FZK), Germany, for large area surface treatment [30]. The two facilities use the same principal set-up as detailed in [31]: electron injector of triode type with a multipoint explosive emission cathode, transport channel, treatment chamber, magnetic system, high-voltage generator, pulse-duration control unit (PDCU), vacuum system, control rack, radiation protection and mechanical support. A schematic of the GESA facility and its capabilities are shown in figure 1, which is typical of such large scale facilities designed to do RTP with electron beams. Recently, Weisenburger [31] presented the surface modification materials using the above facilities and reported that the changes in microstructure led to hardening of gears and increased their wear resistance. A decrease in the oxidation rate of high temperature alloys is also reported. For more details, readers are directed to references in [31] as they cover a range of applications from gears in the automotive industry, turbine blades for energy, cutting tools for manufacturing, to implants and surgical tools in medicine applications.

Hao and Dong [32] demonstrated the use of high current pulsed electron beams (HCPEBs) for surface modification of metallic materials. Their group has actively been studying the HCPEB treatment of pure metals and alloys, such as aluminium and carbon steels [33–38]. A high efficient electron beam of low-energy (10–40 keV), high peak current ($10^2–10^3$ A cm$^{-2}$), with short pulse duration (5 ms) is typically used to generate power density up to $10^8–10^9$ W m$^{-2}$ at the target surface. Recently, the same group has reported the formation of nanostructures on carbon steel using HCPEB [36] with the following beam parameters: electron energy 25 kV, pulse duration 3.5 μs and energy density 4 J cm$^{-2}$, as shown in figure 2. After e-beam treatment, it is found that the modified surface layer can be divided into three zones: the melted layer of depth 3 to 10 µm, the heat and stress effecting zone (10 µm below to about 250 µm) and matrix, where a nanostructure and/or amorphous layer is formed in the near-surface region [36].

Ivanov et al reported the use of low-energy high current electron-beam (LEHCEB) sources as a promising way of developing new highly efficient techniques for the surface treatment of material [39–42]. Proskurovsky [41] showed that for a variety of constructional and tool materials including carbon steel, stainless steel, aluminium alloys, titanium alloys and hard alloys, the surface layers modified as a result of melt quenching show improved strength and...
electrochemical properties. Recently, Koval and Ivanov studied metallocceramic and ceramic materials by electron-beam treatment and observed the formation of submicro- and nanocrystalline multi-phase structures, that result in an increase in physico-mechanical and tribological characteristics of the treated material [42]. Also, recently, Mohanty et al [43] demonstrated polyaniline nanowires formation by electron-beam processing of polyaniline thin films for applications in polymer nanomaterials.

Korenev et al demonstrated the design and development of pulsed low-energy electron sources for material modification applications [44]. New designs aimed at industrial scale material modification technologies are required. Pulsed electron beams for this technology must have a large cross section and good current density uniformity [44].

In summary, the use of electron beams in the surface modification of materials is being actively pursued by several groups for different applications as can be found in the provided references. A variety of e-beam sources were used to treat a wide range of metallic materials and alloys. An improvement in the properties is shown due to the formation of resulting microstructures due to the e-beam treatment. Recently, the use of e-beams for nanostructuring was also demonstrated and it includes even polymer nanomaterials.

2.2. RTP processing using laser beams

Surface modification using lasers also involves melting of the material that interacts with the laser beam followed by the solidification of this molten material. During the cooling cycle (i.e. after the laser irradiation time is over), the solidification of the molten material leads to the formation of different microstructural features depending on several factors such as cooling rate and laser fluence, and while it is possible to produce nanocrystalline thin films using PVD techniques or laser ablation, as demonstrated in [44–48], this review focus is on RTP induced changes in producing the desired micro- or nanostructure on the surface.

The applications of lasers are very widely known and it is beyond the scope of this paper to cover the entire spectrum. Limiting ourselves to the processing of materials, lasers have been the first tool of choice since its invention. Both cw and pulsed lasers have been used for producing microstructures that slowly led the way to producing nanostructures as well. Strutt et al [49] demonstrated the laser surface melting of high speed tool steels using a continuous CO2 laser beam, producing the microstructures that resulted in an appreciable increase in hardness. McCafferty et al [50] demonstrated the use of pulsed laser beams for rapid solidification and melting of an aluminium alloy sample in order to modify the near-surface microstructure, the surface chemistry and the surface topography. The use of pulsed lasers allows the rapid melting of a thin surface layer which is then rapidly solidified, with the bulk providing self-quenching when the incident radiation is removed. This allows greater control in producing the desired microstructures. The RTP processing using laser beams on producing microstructures is similar to the use of e-beams and several research groups [51–63] have obtained microstructures on different kinds of materials (metals, alloys, ceramics) for several applications, including automotive manufacturing, biological, optical and magnetic materials. A schematic of the typical experimental set-up for microstructuring with lasers is given in figure 3. Typically, a laser beam (here, a 4 kW cw Nd: YAG laser (λ = 1064 nm) beam) is focused on to the target surface (alumina ceramic sample (5 × 5 × 2.5 cm) as in figure 3). The target may be mounted on a translation stage that is controlled by CNC programs, allowing precise control of the movements along the X-, Y- and Z-axes. The scan speed and laser fluence are selected appropriately.

The logical progression of the use of lasers is for its use in the production of nanostructures, which is more challenging. The rapid progress in the development of ultra-fast lasers brought life to researchers in material processing applications. The femtosecond lasers have been used for producing nanostructures by (bottom-up approach) laser deposition [46–48] and by (top-down approach) surface nanostructuring of solids [64–68]. Nolte et al [64] and Chimomalgi et al [65] used femtosecond laser pulses in combination with scanning near field optical microscopes or atomic force microscopes to produce nanostructures. Koch et al [66] presented fabrication of nanojets on thin gold films, as shown in figure 4, using a commercial 1 kHz femtosecond laser system delivering 0.9 mJ, 30 fs laser pulses at 800 nm. This work is typical of the nanostructuring that is possible with such techniques.
Vorobyev and Guo [67] showed that nanostructuring is a consequence of femtosecond laser ablation under certain experimental conditions and used the direct approach (not laser plume deposition) to produce nanostructures on copper (see figure 5). They used an amplified Ti–sapphire laser system ($\lambda = 800$ nm, pulse length $\sim 65$ fs, energy $\sim 1$ mJ/pulse, repetition rate: 1 kHz) and the number of laser shots incident on the sample is controlled using an electromechanical shutter. The morphology of nanostructures is dependent on laser fluence as well as number of pulses used. In view of understanding the physical mechanisms involved in material processing, Hertel et al. [68] studied the different ablation phases that are characteristic of pulsed laser structuring of metals. The use of table-top x-ray lasers also for nanoscale ablation was demonstrated by Rocca’s group [69]. Late et al [70] utilized picosecond lasers for synthesis of LiB$_6$ nanostructures. Laser nanostructuring is a rapidly growing area for exciting applications. Henley et al [71] demonstrated the excimer laser nanostructuring of metal thin films with controllable dimensions for the catalytic growth of carbon nanotubes. Ivanov et al [72] investigated the physical mechanisms responsible for the formation of nanobump structures on a surface of a thin metal film irradiated by a tightly focused femtosecond laser pulse using molecular dynamics simulations. They concluded that two-dimensional electron heat conduction provides the conditions for fast cooling of the melted region and rapid solidification of a surface feature generated in the process of hydrodynamic motion of the liquid metal.

In summary, lasers have been an excellent tool of choice for micro- or nanostructuring of materials. Recent advances in laser material processing and modelling provide the ability to control the dimensions of the nanoscale features. Using ultra-fast (pico- or femtosecond) laser pulses that are shorter than the electron–phonon coupling time, one can localize and control the modified surface area, while the surrounding material remains unaffected. These features make lasers particularly attractive for the future of nanostructuring. In addition, the R&D into the development of atto-second laser pulses provides material scientists with more possibilities, as they may be used in controlling the dimensions of nanostructure features with more precision.

### 2.3. RTP processing using ion beams

Ion beams in all forms have been used in producing nanostructures, either in the top-down or bottom-up approach. A review of the use of ion beams for producing nanostructures is provided by Avasthi and Pivin [73] wherein synthesis of nanostructures by ion implantation, ion-beam mixing and nanostructures under the effect of electronic excitations is very well reviewed. Frost et al. [74, 75] utilized low-energy ion-beam sputtering to produce self-organized nanostructures, while recently Ghose [76] utilized off-angle ion-beam sputtering for development of nanostructures in polycrystalline metal films. The use of focused ion beams for nanostructures is also reported in [77, 78].

With the focus of the current review being variants of RTP, the use of ion beams in this regard is given here. RTP with intense ion beams is capable of rapidly heating and cooling the near-surface region of treated materials including metals, ceramics, polymers and mixed materials. In 1989, Pogrebnjak et al. [79, 80] reviewed the use of high-power ion beams (HIIBs) for the surface treatment of metals and alloys, and have shown that these modified surfaces exhibit increased microhardness, abrasive and cutting wear resistance. Piekszewski and Langner [81] reviewed the experiments
illustrating the modification of the surface properties of semiconductors, metals and ceramics using high intensity pulsed ion beams (HIPIBs) and their group’s work can be found in [82–85]. RTP with ions leads to altered microstructures, reduced grain size, metastable phase formation, and improved mechanical and other properties in the treated region.

Stinnett et al [86] presented a new, commercial-scale thermal surface treatment technology called Ion Beam Surface Treatment (IBEST) based on the availability of high average power (5–500 kW) pulsed ion beams at 0.5–1 MeV energies. The technique uses high-energy, pulsed (typically <100 ns) ion beams to directly deposit energy in the top 2–20 µm of the surface of any material as shown in figure 6. The depth of the treatment is controllable by varying the ion energy and species. Similarly, Rej et al [87] reviewed the application of intense pulsed ion beams (IPIBs) for the surface treatment and coating of materials. The short range (0.1–10 µm) and high-energy density (1–50 J cm⁻²) of these short-pulsed (<1 µs) beams with ion currents (5–50 kA), and energies (100–1000 keV) make them an ideal RTP source that induces rapid melt and solidification at up to 10¹⁰ K s⁻¹, causing amorphous layer formation and the production of nonequilibrium microstructures. Several research groups have used IPIBs for material modification [88–93] for different applications. Renk et al [94] reviewed material modification using intense beams and have shown that RTP with ion beams is quite promising for large scale commercial use due to the high-specific ion energy deposition (J cm⁻³) without reflection, and to the relative efficiency and low cost of the pulsed power ion-beam drivers compared with other high-kinetic energy alternatives. An example of improvement in material properties, wear resistance of stainless steel, after ion-beam treatment in the IBEST facility is illustrated in figure 7.

In summary, ion beams have been used as an effective RTP source for microstructuring of materials. While ion beams are more common in synthesizing nanostructures using the bottom-up approach, the top-down RTP nanostructuring of materials is not seen much as it places higher demands on the ion-beam design and development. While this is a drawback from the nanomanufacturing point of view, the advantages in ion beams lie in the inherent efficiency of the beam generation and relative compactness of the beam source compared with a laser source. This allows the ion-beam techniques to be potentially scaled to an industrial process. Future research and development into focused ion-beam sources might allow nanostructuring of materials in an industrial scale.

3. Pulsed plasma exposures using Z-pinch plasma source

Changing the morphology of a surface on the nanoscale can dramatically alter its surface properties. The appropriate changes can eliminate reflection, reduce wear, or make the surface itself act as a catalyst. These tailored surfaces are produced through the input of significant energy (0.1 to 5 J) in very short time-scales (~10 ns or shorter). We have seen the use of electron beams, ion beams and lasers as a tool for material modification in earlier sections. Here, the use of a high-density, high-charge-state pulsed plasma source facility, located in the Center for Plasma Material Interactions at the University of Illinois at Urbana Champaign, for micro/nanostructuring of surfaces is described. Although, pulsed plasma sources have been available for quite some time, their application to material modification has been seen only recently. Garkusha [95–97] and their group at the National Science Center ‘Kharkiv Institute of Physics and Technology’ (NSC KIPT) employed ultra-short (10⁻⁶ s) energetic plasma pulses to tailor the material surface properties. They reported a four times increase in surface hardness even for previously quenched steels, and a four to 10 times improvement in wear resistance and enhancement of corrosion and erosion characteristics. Similar effort was also undertaken by Rawat et al using the ions from a dense plasma focus device to induce changes in morphological, structural, mechanical and optical properties of thin films and bulk materials [98–101].

Here, we report a unique plasma-based technique to rapidly expose surfaces to a very energetic, high-density, high-charge-state (30 eV, 10²⁰ cm⁻³⁻¹, ionization states up to +12) plasma. Each individual pulse lasts only 10 ns, but deposits 1 to 5 J of energy. The plasma can be made from any gas, allowing the possibility of incorporating a number of species
Figure 8. Schematic (a) and photograph (b) of the XTS 13-35 EUV Z-Pinch at the University of Illinois. The device is capable of operation up to 1.5 kHz, 8 J per 10 ns pulse. The pinch rapidly expands so energy density can be controlled through sample placement.

Figure 9. Schematic of the experimental set-up for micro/nanotexturing of surfaces.

into the material being treated. The high-density high-charge-state pulsed plasma source is a source of energetic ions, neutrals and photons, which are all responsible for depositing energy into a thin layer of any surface. The depth of modification and the resultant microstructure is controlled by the plasma parameters. The rapid quenching due to the bulk material produces a fine grained layer containing microstructures or nanostructures that exhibit superior material properties. This technology could be used for any material including ceramics, metals or polymers.

3.1. Experimental set-up

Figure 8 shows the discharge-produced plasma source. It is a Z-pinch used as a source for EUV lithography. We are the first to intentionally use this plasma to modify material surfaces. The plasma produces bursts of EUV (13.5 nm) light, but only 3% or less of the energy goes into such photons. The rest goes into plasma creation of energetic ions, electrons and a wide range of photon energies [102] that are all utilized here for surface tailoring.

Figure 9 shows the schematic of the experimental set-up. A sample is loaded using a load lock and transfer arm and in the current set-up the sample is positioned at approximately 2 cm away from the Z-pinch plasma. The energy density on the target can be controlled through this target sample placement. Several diagnostics were used to characterize the plasma source and are not covered here as it is not the subject of the review. The proof-of-concept experiments were performed on aluminium and tungsten samples. The sample preparation procedure and analysis can be found in [103].

3.2. Results

3.2.1. Evidence of micro/nanostructures. The idea behind modifying the surface grain structure with a high-power pulse is to suppress nucleation of crystalline phases, so that an amorphous surface structure results momentarily. This requires extremely rapid cooling rates to bring the temperature down below the glass transition level, before the onset of crystal nucleation. At the right energy level, nanocrystalline structures are created. Samples of aluminium and tungsten were treated with the Z-pinch plasma source in the XCEED facility and SEM images show a clear evidence of formation of nonequilibrium microstructures consisting of nanocrystalline and/or metastable phases. Figure 10 shows the SEM images of an aluminium sample exposed to N2 pinch plasma for 500 pulses, where in fine nanograins on the surface can be seen. Figure 11 shows the SEM image of a treated tungsten sample which was exposed for 45 s to the argon plasma at 50 Hz operation, for a longer time compared with the Al sample. The resultant formation of microstructures can be seen from
3.2.2. Hardness measurements. For hardness measurements, we compared the performance of pulsed plasma treated surfaces with untreated surfaces. Figure 12 shows an increase in surface hardness of the tungsten sample in all three zones of the treated tungsten sample. Similarly, hardness measurements have been performed on Al samples as well. Two separate experiments were conducted to test the effect of nitriding the sample. One sample is exposed to Ar plasma and the other is exposed to the nitrogen plasma and the results are presented in figure 13. The results have shown that the hardness is increased by a decrease in the grain size of Al as evidenced by the 100 shots exposure. However, as the exposures are increased to more shots, the formation of bubbles and porous structures resulted in a decrease of hardness. The evidence of AlN formation can be seen from the fact that the hardness increased as opposed to the Ar plasma exposure, for longer exposures with N\textsubscript{2} plasma. While only a summary of results is presented here, the interested reader is encouraged to look into future publications.

In summary, the capability to produce very energetic, high-density plasma is enabling us to develop a new thermal surface treatment technology. In this method, more energy could be coupled into the material compared with laser processing where there might be losses due to reflection and transparency. This new technology incorporates ion implantation simultaneously with rapid surface thermal treatment. In addition, this method inherently allows us to add species to the surface during processing, which might enhance the properties of the surface of the material. For example, nitriding, boronizing or alloying can be performed.

4. Summary and conclusions

Tailoring surfaces of materials has been an active area of research in the field of material science. The ability to modify the properties of the surface without altering the properties of the bulk has given rise to many scientific, technological and biological applications. For example, production of nanostructures on the surfaces of solids improves their physical and mechanical properties. Nanomaterials is rapidly advancing for the unique benefits it offers to the material world. They are used in the fabrication of optical devices, magnetic media, electronic devices and bio-compatible surfaces. Each of the papers discussed in the review includes the production of nanostructures for several applications such as catalysis, thermoelectric devices, magnetic materials, drug delivery and energy applications. Several advances in materials research have been made due to the wide array of tools currently available for the processing of materials: plasmas, electron beams, ion beams and lasers. These technological developments in the tools of choice, in addition to the advances made in nanomaterials research, have led to the development of micro/nanostructures on surfaces with superior properties.

The RTP of materials allows a unique pathway to synthesize micro/nanostructures on the surface of a material, thereby enhancing its properties. Each tool described in the review offers unique advantages and disadvantages, and the optimal tool of choice depends on the type of application. Overall, the main advantage of the RTP of materials is the ability to produce nanostructures directly on the material itself and the simplicity in the experimental set-up. It can be used to treat almost all materials including metals, semiconductors, polymers, etc. In addition, the ability to control energy fluxes on the material will allow greater control of the size of nanostructures produced. Furthermore, RTP offers the possibility to produce three-dimensional nanostructures as well. Another advantage of nanostructuring by RTP methods...
is the ability to modify material without significant loss of material, thus making it effective and a commercially viable process.

Of particular mention is the additional advantage that plasmas provide to fabricate nanostructures as presented in section 3. The use of energetic and highly dense plasma offers efficient coupling of energy into the material compared with other RTP methods. In addition, plasma makes use of the energetic ions and incorporates ion implantation simultaneously with rapid surface thermal treatment. This also eliminates the need for the additional annealing methods required to improve the properties of nanostructures. Also, the properties of the surface of the material can be further enhanced by adding dopant-like species, which can be done inherently with the plasma processing method described here. The advantages of ion-beam rapid thermal processing combined with a material alloying capability make pulsed plasma sources an attractive technology for future surface treatment applications.

However, careful control is required to fabricate these nanostructures with a high degree of control over their size, shape and composition distributions. Optimizing this parameter space is extremely challenging, considering that these nanostructures have to be produced in large scale specifically tailored for a particular application. Hence, in order to realize the full potential of these processing methods more research and development is needed to fabricate these structures at cost-effective production suitable for industrial implementation. The research should include understanding the effect of the parameters (such as energy required, pulse duration, etc) of the RTP sources on material surface using surface characterization techniques. As these relations are well established, new cost-effective sources could be developed for the commercial fabrication of unique nanostructures on any material surface.

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