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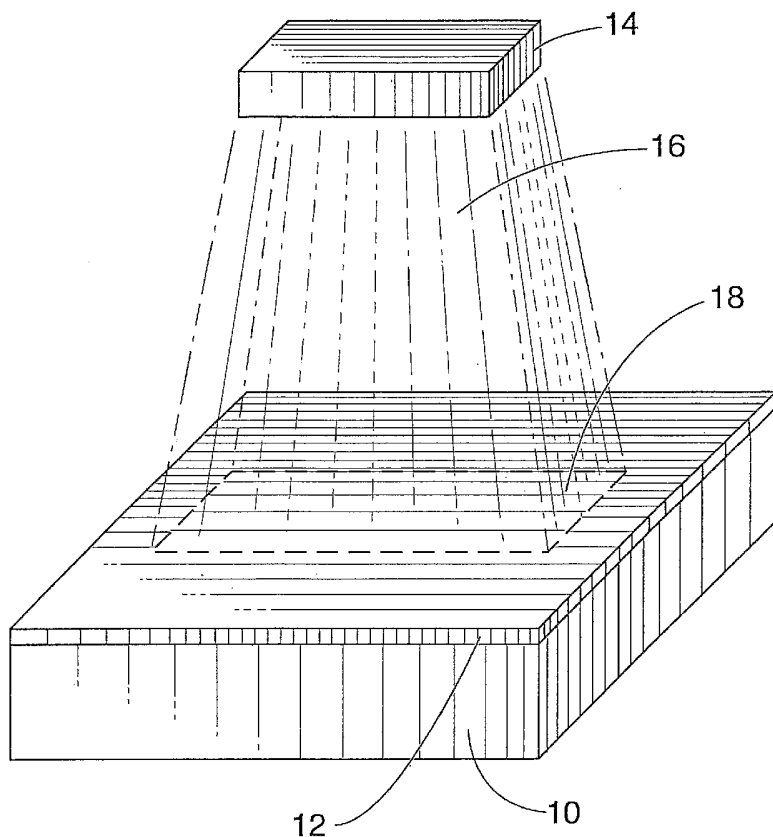
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(54) Title: PULSE THERMAL PROCESSING OF FUNCTIONAL MATERIALS USING DIRECTED PLASMA ARC



(57) Abstract: A method of thermally processing a material includes the steps of providing an article having a surface film disposed on a substrate, and exposing the thin film to at least one incident pulse of infrared comprising radiation at a power density of at least 0.1 kW/cm² emitted from a directed plasma arc to thermally process the thin film. The at least one pulse has a duration of no more than 10 s. The method provides a radiation intensity and spectrum of radiation capable of heating the surface film to the desired temperature while allowing the substrate to remain at a lower temperature. This feature permits use of substrates that generally are not high temperature tolerant, such as certain polymer substrates.



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PULSE THERMAL PROCESSING OF FUNCTIONAL MATERIALS USING DIRECTED PLASMA ARC

FIELD OF THE INVENTION

[0001] The present invention relates to methods of rapidly processing functional materials, and more particularly to rapidly processing functional layers on temperature-sensitive substrates by exposure to high power density pulsed radiation emitted from a directed plasma arc (DPA).

BACKGROUND OF THE INVENTION

[0002] Known methods of thermally processing (annealing and sintering, for example) functional materials must generally be performed at elevated temperatures and take several hours, thus a substrate that supports a functional material must be capable of withstanding the requisite processing environment. In order to advance the technology of thin-film and nanoparticle devices, more attractive substrates that are light-weight and flexible must be considered. In many cases, substrates that would fulfill such criterion are temperature-sensitive and are not able to withstand the processing environment of a conventional furnace. Such temperature-sensitive substrates – for example, low melting point, light-weight metals and flexible polymers, cannot withstand the high temperatures necessary for processing the thin-film surface layer. Moreover, there is a need for larger area processing and shorter processing times than that available with conventional processes.

SUMMARY OF THE INVENTION

[0003] In accordance with one aspect of the present invention, a method of thermally processing a material, comprises the steps of providing an article having a surface film disposed on a substrate; exposing the thin film to at least one incident pulse of infrared comprising radiation at a power density of at least 0.1 kW/cm^2 emitted from a directed plasma arc to thermally process the thin film. The at least one pulse has a duration of no more than 10 s. As used herein, the phrase "infrared comprising radiation" refers to a radiation pulse that a least a portion thereof is infrared radiation. The pulse can have a duration in the range of 1 μs to 500 ms. The exposing step can comprise at least two pulses of infrared comprising light emitted

from a directed plasma arc, said pulses having a periodicity of no more than 60 s, such as in the range of 1 μ s to 30 s.

[0004] The surface film can comprise at least one functional material selected from the group consisting of a nanoparticle material, a thin-film material, and a thick-film material. The surface film can comprise a self-assembled nanoparticle magnetic media system, such as based on FePt, FePtAu, and CoPt. in another embodiment, the surface film comprises a photovoltaic, such as Cu-In-Ga-Se or Cu-In-Se.

[0005] The surface layer comprises carbon nanotubes. in another embodiment of the invention, The surface layer comprises at least one material selected from the group consisting of a transistor material, and a battery material. The transistor material can comprise at least one material selected from the group consisting of silicon, germanium, a germanium-silicon alloy, and indium-doped titanium oxide. The substrate can be a temperature-sensitive material selected from the group consisting of a biomaterial, a polymer and a resin. The power density can be at least 0.5 kW/cm², such as 1.0 kW/cm². The temperature of said surface film can reaches at least 2,500 °C during the method, such as 3,000 °C, with the substrate being at a significantly lower temperature, such as < 600 °C.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] A fuller understanding of the present invention and the features and benefits thereof will be accomplished upon review of the following detailed description together with the accompanying drawing, in which:

[0007] Fig. 1 is a schematic illustration of a process being carried out in accordance with one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0008] Pulsed energy from a directed, high density infrared plasma arc lamp, referred to hereinafter by the term "directed plasma arc" (DPA) is a preferable used in the present invention. A suitable device that produces the necessary DPA is described in U.S. Patent No. 4,937,490 (referenced above). The DPA can supply large power densities, up to 20 kW/cm², for example, depending on the setup, simultaneously over large areas, for example, 300 cm², in short time frames in a controlled manner.

[0009] Another generally suitable high density plasma arc lamp is produced by Vortek, Inc. of Vancouver, Canada. The plasma is contained in a quartz tube and the resulting radiation is directed to the surface film using elliptical reflectors. This particular plasma-based furnace operates as a line-focus type system, whereby the surface film is treated by scanning radiation across its surface. Minimal convective currents are produced in the heated material because the uniform area heated by such a lamp alone is generally at least 100 cm², such as approximately 3 cm by 35 cm. Scanning the lamp over the surface film may be used to increase the size of the uniformly heated area. The system can also include substrate cooling.

[0010] Any radiation source that produces sufficient radiation intensity and a spectrum of radiation capable of heating the surface of the surface film to the desired temperature while allowing the substrate to remain at a lower temperature can be used for the invention. This feature permits use of substrates that generally are not high temperature tolerant, such as certain polymer substrates. The substrate temperature can be 100 °C to 800 °C (or more) cooler than the temperature of the surface film. In one embodiment of the invention where ionized gas that comprises the plasma is Ar, the emission is primarily infrared, emitted radiation wavelengths ranging from approximately 0.2 μm to 1.4 μm. Since 0.2 μm to 0.39 μm wavelength radiation is characterized as ultraviolet radiation, 0.39 μm to 0.78 μm visible radiation and 0.78 μm to 1.41 μm infrared radiation, ultraviolet radiation, visible radiation and infrared radiation can all be simultaneously radiated by the radiation source used in one embodiment of the invention. Different gases can shift that output. The spectral output can also be filtered so that only a portion of the spectral output is exposed to the specimen.

[0011] Shorter pulse lengths, such as < 1 second, such as < 1 msec allow for decreasing the integrated heat load applied to the surface film coated substrate specimen. Also, the short pulse times allow for a transient (non-equilibrium) heat transfer regime. By maintaining a transient heating process, the specimen does not undergo heat soaking, which would occur with longer pulse times. The high density plasma arc lamp is also well suited for being scaled so that the entire desired processing footprint is processed all at once. The preferred large area processing capability offers more microstructural uniformity and minimizes residual stresses within the processed layer.

[0012] The heating process utilizing the pulsed DPA is capable of quickly delivering large amounts of heat over large surface areas with little or no deleterious influence upon subsurface (e.g. substrate) compositions, such as phase change, melting or decomposition. Pulses of energy from the DPA can be of as short in duration and/or periodicity as the

physical limitations of the device that produces the DPA, preferably in a manner that allows precise control various process parameters, such as work-piece surface temperature, temperature programming, and the like. The process can be carried out in a vacuum, air, liquid, inert fluid, reactive fluid, or generally any type of environment needed for processing.

[0013] In accordance with the present invention, the duration of pulse of radiation from the DPA can be any duration within the range of 0.5 μ s (microsecond) to 10 s (second), inclusive, with typical pulse durations being, for example, 0.5 μ s, 0.75 μ s, 1 μ s, 2.5 μ s, 5 μ s, 10 μ s, 25 μ s, 50 μ s, 75 μ s, 100 μ s, 250 μ s, 500 μ s, 750 μ s, 1 ms, 2.5 ms, 5 ms, 10 ms, 25 ms, 50 ms, 75 ms, 100 ms, 250 ms, 500 ms, 750 ms, 1 s, 2.5 s, 5 s, and 10 s. Pulse duration can be held to a single duration throughout the process, or it can be varied as desired within the defined range.

[0014] In accordance with the present invention, the periodicity (time interval between the end of one pulse and the beginning of the next pulse) can be any periodicity within the range of 0.500 ns to 60 s, inclusive, with typical periodicities being, for example, 0.5 μ s, 0.75 μ s, 1 μ s, 2.5 μ s, 5 μ s, 10 μ s, 25 μ s, 50 μ s, 75 μ s, 100 μ s, 250 μ s, 500 μ s, 750 μ s, 1 ms, 2.5 ms, 5 ms, 10 ms, 25 ms, 50 ms, 75 ms, 100 ms, 250 ms, 500 ms, 750 ms, 1 s, 2.5 s, 5 s, 10 s, 20 s, 30 s, 45s, and 60 s. Pulse periodicity can be held to a single periodicity throughout the process, or it can be varied as desired within the defined range.

[0015] Referring to Fig. 1, a typical work-piece (substrate) 10 has a surface coating 12. A DPA 14 directs a pulsed beam of preferably primarily IR light 16 onto an area 18 of the coating 12 to thermally process the coating 12.

[0016] The high-temperature and short exposure times associated with DPA pulse thermal processing make it possible to process, for example, crystallization of amorphous films, recrystallization and grain growth, and grain boundary refinement of crystalline films, phase transformation and sintering, controlled sintering and other thin-film and nanoparticle processing, without excessive heating of the substrate. Functional materials can thus be processed on temperature-sensitive substrates so that the temperature-sensitive substrate is not deleteriously affected by the incident pulsed energy.

[0017] The term "temperature-sensitive" as used herein means that, at a temperature equal to or less than the temperature at which a functional surface film material coated thereon is processed, at least a portion of the substrate melts, decomposes, reacts, sublimates, interdiffuses with the functional material, or otherwise changes physically or chemically in a way that is deleterious to its usefulness as a substrate. A substrate can be monolithic or it can be layered, any layer of which can be temperature-sensitive.

[0018] Some examples of functional materials include, but are not limited to nanoparticle materials, thin-film materials, thick-film materials, and the like. Some examples of temperature-sensitive substrates include, but are not limited to biomaterials, polymers, resins, other organic materials, metals, ceramics, semiconductors, and other inorganic materials.

[0019] A typical process may proceed as is as follows:

[0020] 1. A functional material is deposited or grown on a substrate.

[0021] 2. The functional material is exposed the DPA at a low power level in order to preheat the thin-film/substrate system, if needed. This low power level can be maintained for sufficient time to allow thermal equilibrium to occur.

[0022] 3. The DPA is pulsed at a preselected higher level power, and for a preselected pulse duration.

[0023] 4. The DPA is brought back down to the preheat power level and held for a preselected period of time.

[0024] 5. Steps 3 and 4 are repeated, applying large amounts of energy to the functional material in short bursts over large areas.

[0025] The temperature of the functional material can be raised at a controlled rate of up to several orders of magnitude higher than currently available with tungsten-halogen based infrared radiant heating sources. Time at maximum temperature can be minimized.

[0026] The present invention is suitable for at least the following specific exemplary applications:

Nanoparticle Systems

[0027] Some nanoparticle systems require critical heat treating steps, which often present the challenge of processing these systems, and processing them on a temperature-sensitive substrate. It is often necessary to control the sintering process of the nanoparticles. In some instances it may be necessary to prevent sintering altogether while performing some other process (for example, phase change) within the nanoparticles. Other instances require varying degrees of sintering so that there is control over the density of the nanoparticle system.

[0028] The present invention is applicable to self-assembled nanoparticle magnetic media systems such as FePt, FePtAu, and CoPt, for example. As-deposited nanoparticles must undergo phase transformation with minimal sintering in order to obtain the desired magnetic properties. For example, FePt thin films for magnetic media can have a thickness of 20-100

nm where the thin film is processed with pulses of heat energy from a plasma arc lamp. Currently, data densities of 30-50 GBit/in² are attainable. With the aid of the present invention, data densities of 1 TBit/in² are attainable by decreasing the grain size, and also the number of grains per bit. With the aid of the present invention, grain size distribution can be reduced for the current state-of-the-art of 25% to no more than 10%, and even less than 5% under optimized conditions. The present invention further applies to PtMn thin films for giant magnetoresistance (GMR) read heads for magnetic media where the film is processed at elevated temperatures without introducing grain growth to the thin film and without measurably altering the properties of the underlying substrate.

[0029] In an optimized self-assembled FePt nanoparticle magnetic media system made the average nanoparticle size is about 3.5 nm and with an organic coating of approximately 2nm, with grain size distribution of no more than 5%. The process defined herein heats the organic coating to affect a phase change without altering the properties of the FePT nanoparticle. Further, self-assembly occurs during solvent evaporation, controlled by steric repulsive forces (usually due to an organic surfactant coating that is often used) and natural attractive forces and interactions of the nanoparticles. Self-assembly preferably results in a closed-packed structure with a center-to-center distance of about 8 nm.

[0030] Processing of the self-assembled FePt nanoparticle structure in accordance with the present invention can promote thermal annealing while inhibiting sintering. Moreover, breakdown of the organic surfactant is minimized, preventing agglomeration of the nanoparticles. The result is phase transformation of the nanoparticles from a disordered face-centered-cubic (FCC) structure to an ordered L1₀ face-centered-tetragonal (FCT) structure. This structure is characterized by optimal magnetic properties for high density data storage.

[0031] The present invention is applicable to nanoparticle photovoltaic systems such as a Cu-In-Ga-Se (CIGS) and Cu-In-Se (CIS) systems, for example. The CIGS system has shown the highest efficiencies for next generation solar cells. One problem with sputtered thin-film production of the CIGS system is that there is little control of the composition over large areas. By utilizing a screen printing process to deposit a CIGS, or some other similar system, nanoparticle composition there is more compositional control over large areas. In order for the nanoparticle system to achieve high collection efficiencies the nanoparticles need to undergo a sintering process that might require temperatures in the range of 500°C to 700°C. Obviously, most polymer or other temperature-sensitive substrates cannot withstand such an environment, unless they were processed utilizing the present invention procedure. Utilizing

the present invention, the density of the nanoparticle system can be controlled to full density on temperature-sensitive substrates.

[0032] The present invention is applicable to nanotube systems such as carbon and FeMo nanotube systems, for example. Processing in accordance with the present invention can induce rapid nucleation of single-walled nanotubes. By starting with nanoparticles and rapidly nucleating nanotubes from those nanoparticles, single-walled nanotubes will generally be the predominant product. However, if the nanoparticles are allowed to sinter prior to nucleation of the nanotubes, then the starting volume for the nanotube has increased and the product will predominantly be multi-walled nanotubes. Thus, by rapidly nucleating the nanotubes from the nanoparticles without sintering occurring, predominantly single-walled nanotubes can be produced in accordance with the present invention.

Thin-film systems

[0033] The present invention is useful for processing various thin-film materials on any type of substrate. These annealing processes can be, but not limited to, recrystallization of crystalline films, crystallization of amorphous films, grain growth, and grain boundary refinement. Examples of applications in which these annealing processes provide benefits are thin-film photovoltaic materials where large grains and refined grain boundaries are needed to improve device efficiency.

[0034] For example, ribbon grown polycrystalline silicon, which is cheaper than wafer processed silicon but not as pure as wafer processed silicon, can be purified with high thermal energy pulses. Pulsing at high energies with a plasma arc lamp can drive hydrogen from a SiNx anti-reflective layer into the film-fed-grown ribbon silicon to passivate defects to result in SiNx-induced hydrogen passivation. Such high energy pulse processing can remove impurities from the grain boundaries while minimizing diffusion within the bulk and increase the metallurgical bonds of silver and aluminum for front- and back-side contacts to further increase efficiencies.

[0035] In another example, Photovoltaic material systems, such as thin film copper indium gallium diselenide (CIGS) and amorphous silicon can be processed efficiently using high heat energy pulses. In the past, the processing of such materials using sputtering techniques lead to non-uniform compositions and post deposition annealing needed to be performed in a selenium environment to maintain a constant stoichiometry. The processing of CIGS using pulsed high heat energies results in purified grain boundaries with less impurities and defects and can increase collection efficiencies by 50%. Further, CIGS can be

processed without a selenium environment with no to a negligible loss of selenium. Still further, CIGS alloys can be created using high heat energy pulses from the plasma arc lamp where nanoparticles are sintered to a sheet. By way of an example, such sintering can occur to a polymer substrate.

[0036] In another example, amorphous silicon can be processed. The high heat energy pulsing plasma arc lamp introduces a nano- or micro-crystalline silicon phase within the amorphous matrix by solid-phase-crystallization to increase collection efficiencies by up to 50%. In contrast to processing with a laser, the plasma arc lamp according to the invention provides for processing on polymers over large areas which reduces microstructural variations leading to uniform optical and electrical properties. Still further, pulsing high heat energies can be used to process on polymer substrates, which previously degraded under other processing techniques because the upper working temperature of the polymer substrates is approximately 400C and the films are processed at approximately temperatures above 600C. Along those same lines, a Gratzel Cell, such as TiO₂ nanoparticles with sensitizing dye/electrolyte, can be processed with high heat energy pulses to partially sinter nanoparticles to increase electrical conductivity reaching temperatures above 550C. Collection efficiencies can be increased by approximately 30-50%.

[0037] In still another example, high heat energy processing using a directed plasma arc lamp can result in the improvement of crystallization of hydrogenated amorphous silicon (a-Si:H). The processing introduces a nanocrystalline structure in the amorphous phase in order to increase electron mobility. The amorphous silicon can be processed on a flexible polymer substrates and result in a more uniform material properties as compared to the rastering technique used in connection with lasers which can result in poor electrical and optical properties and large residual stresses. Pulse thermal processing allows for processing large areas at a given time thus providing uniform microstructures leading to uniform electrical and optical properties and minimal residual stresses.

[0038] Other applications of the present invention include thin-film batteries, thin-film transistors (TFT), and other microelectronic applications, many of which generally require crystallization of an amorphous thin-film and/or improved grain growth. Examples of thin-film materials include lithium-containing thin-film battery components, amorphous silicon, germanium, germanium-silicon alloys, and indium-doped titanium oxide.

[0039] While there has been shown and described what are at present considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various

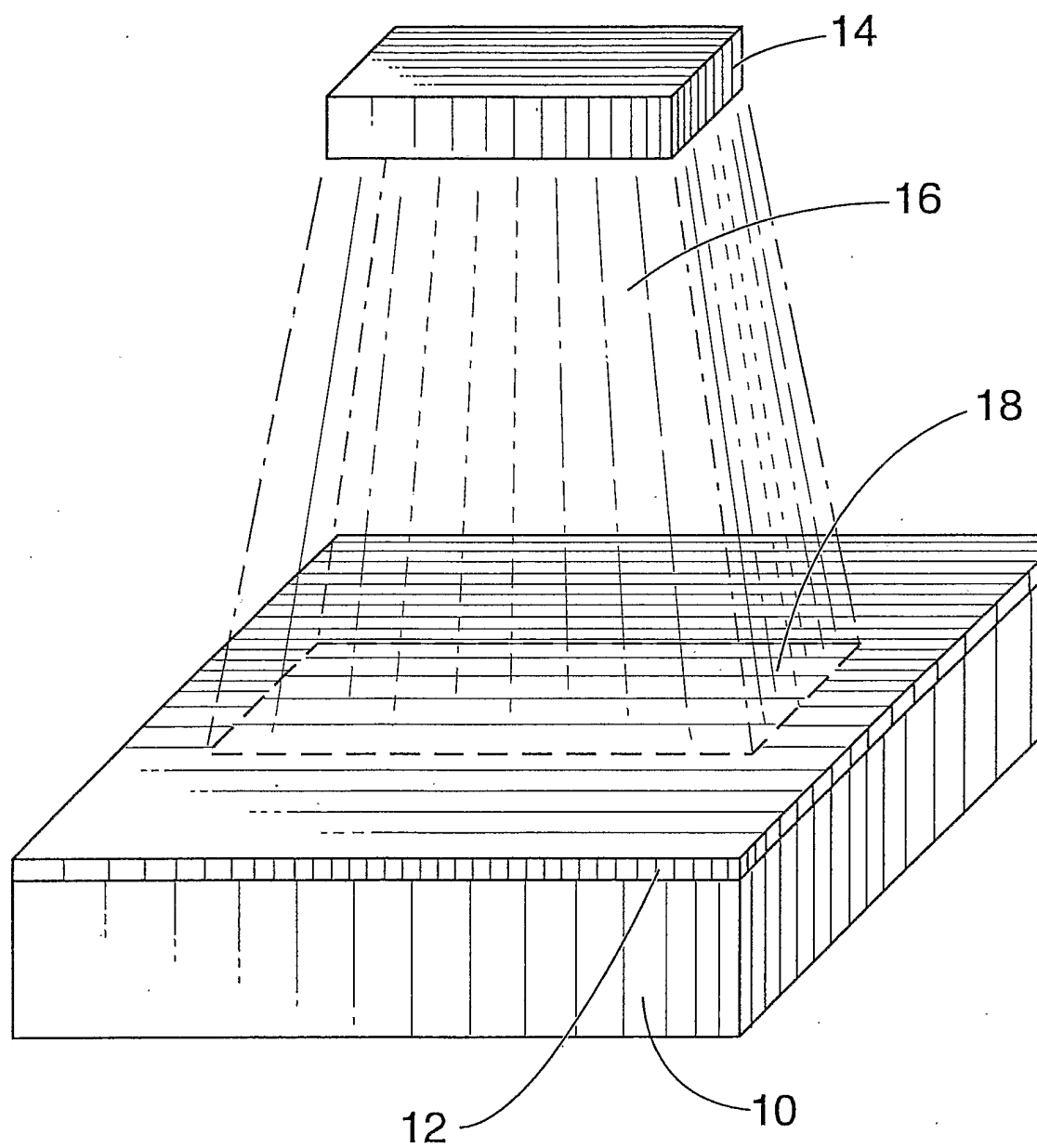
changes and modifications can be prepared therein without departing from the scope of the inventions defined by the appended claims.

CLAIMS

What is claimed is:

1. A method of thermally processing a material, comprising the steps of:
providing an article having a surface film disposed on a substrate;
exposing said thin film to at least one incident pulse of infrared comprising radiation at a power density of at least 0.1 kW/cm^2 emitted from a directed plasma arc to thermally process said thin film, said pulse having a duration of no more than 10 s.
2. The method of claim 1, wherein said pulse has a duration in the range of 1 μs to 500 ms.
3. The method of claim 1, wherein said at least one incident pulse comprises at least two pulses of infrared comprising light emitted from a directed plasma arc, said pulses having a periodicity of no more than 60 s.
4. The method of claim 3, wherein said pulses have a periodicity in the range of 1 μs to 30 s.
5. The method of claim 1, wherein said surface film comprises at least one functional material selected from the group consisting of a nanoparticle material, a thin-film material, and a thick-film material.
6. The method of claim 1, wherein said surface film comprises a self-assembled nanoparticle magnetic media system.
7. The method of claim 6, wherein said self-assembled nanoparticle magnetic media system further comprises at least one material selected from the group consisting of FePt, FePtAu, and CoPt.
8. The method of claim 1, wherein said surface film comprises a photovoltaic.
9. The method of claim 8, wherein photovoltaic further comprises at least one material selected from the group consisting of Cu-In-Ga-Se and Cu-In-Se.

10. The method of claim 1, wherein said surface layer comprises carbon nanotubes.
11. The method of claim 1, wherein said surface layer comprises at least one material selected from the group consisting of a transistor material, and a battery material.
12. The method of claim 11, wherein said transistor material further comprises at least one material selected from the group consisting of silicon, germanium, a germanium-silicon alloy, and indium-doped titanium oxide.
13. The method of claim 1, wherein said substrate is a temperature-sensitive material selected from the group consisting of a biomaterial, a polymer and a resin.
14. The method of claim 1, wherein said power density of at least 0.5 kW/cm^2 .
15. The method of claim 1, wherein said power density is at least 1.0 kW/cm^2 .
16. The method of claim 1, wherein a temperature of said surface film reaches at least $2,500^\circ\text{C}$ during said method.

**FIG. 1**