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Laser polarization-assisted diffusion for modifying electromagnetic properties of metals

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ABSTARCT

Laser diffusion has previously been studied to incorporate dopants in semiconductors and to carburize steel for surface hardening without melting the substrate, among others. The optical and electromagnetic properties of materials can also be modified by this diffusion method to tailor the material response at different frequencies of the electromagnetic spectrum. Platinum atoms have been diffused into titanium and tantalum sheets by a laser chemical vapor diffusion method using a metallorganic compound of platinum and laser beams of different polarizations. Thermal decomposition of the precursor at the laser-heated spot on the surface of the substrate generates platinum atoms that diffuse into the substrate, producing laser-platinized samples. The transmittances of the samples are determined by measuring the strength of the transmitted magnetic field oscillating at 63.86 MHz. The laser-platinized samples produced by linearly polarized lasers exhibit higher transmittances than the samples obtained by using azimuthally polarized lasers.

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1. Introduction

The optical and electromagnetic properties of materials at different frequencies of the electromagnetic spectrum have been widely used in many applications such as communications, imaging and remote sensing. Laser chemical vapor diffusion has been used to dope semiconductors for fabricating semiconductor devices such as light-emitting diodes, [1] gas sensors [2] and transistors, [3] and to modify the surface chemistry for improved mechanical properties such as hardness. In this diffusion process, the substrate is generally heated with a laser beam in a vacuum chamber containing the vapor of a suitable metallorganic precursor of the dopant atoms, resulting in thermal decomposition of the precursor, production of the dopant atoms and subsequent diffusion of the atoms into the substrate. The advantage of this process is that the rapid heating and cooling inherent in laser processing provides a nonequilibrium diffusion mechanism to achieve higher dopant concentration in the substrate than the solid solubility limit of the substrate [1]. Similar to altering the properties of semiconductors, the electromagnetic properties of metals can also be modified by the laser chemical vapor diffusion method to tailor the material response, such as reflection and transmission, at different frequencies of the electromagnetic spectrum [4]. Laser heating can be used to incorporate diffusant atoms into the substrate. It can also be used to induce solid state diffusion among the constituent atoms of the substrate to form new crystalline phases for enhancing material properties.

To produce a diffused layer of impurities in metals, the conventional solid state diffusion process, which occurs under isothermal conditions in a furnace, is not applicable in many cases where the mechanical properties such as the yield and fatigue strengths are affected due to prolonged exposure to high temperatures. The laser diffusion technique is a non-isothermal solid state diffusion process without melting the substrate. Diffusion can be accomplished at much higher localized temperatures at shorter durations than in the conventional furnace-based diffusion process. This non-isothermal, localized high-temperature diffusion mechanism increases the diffusion coefficient and concentration of impurities with minimal changes in the mechanical properties of the substrate. The laser irradiance, laser-substrate interaction time and reflectivity of the substrate are generally studied for modifying the properties of materials by laser heating. Polarization is another important property of lasers that can be useful for changing the structures of materials.

Laser polarization represents the direction traced by the tip of the oscillating electric field of the laser over one period of oscillation on a plane perpendicular to the direction of propagation of the laser.

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Petring et al. [5] showed that the absorptivity of the workpiece depends on polarization in laser cutting. Niziev and Nesterov [6] studied the efficiency of cutting as a function of laser polarization and achieved higher efficiency with a radially polarized laser than with a linearly or circularly polarized laser for cutting metal sheets with large aspect ratios. Ho [7] calculated the absorbed laser energy for keyhole welding and drilling applications where the laser undergoes single reflection in a certain region of the cavity or multiple reflections in other regions. The absorbed energy per unit area is the highest for *s*-polarization in the single reflection zone, whereas the total absorbed energy is the highest for *p*-polarization in the multiple reflection zone. The polarization allows to modify the properties of material by two mechanisms: (i) a thermal effect in which the polarization-dependent absorption of laser energy affects the temperature distribution in the substrate and, consequently, the impurities are thermally activated for the diffusion process, and (ii) a phonon effect in which the electric field of the laser can restrict the vibrational motions of the impurities to certain directions and, therefore, the diffusant atoms migrate in an organized manner instead of moving randomly. Artsimovich et al. [8] obtained higher diffusion coefficient of oxygen in Si with a laser beam of polarization parallel to the Si–O–Si bonds. Pavlovich [9] presented a theory to explain the enhanced diffusion coefficient of oxygen in Si and concluded that the enhancement occurs when the quantum of energy and the vibrational energy of Si lattice are comparable and the direction of polarization is parallel to the direction of antisymmetric vibration of oxygen atoms along $<111>$.

2. Experimental studies

2.1. Laser platinum diffusion

To incorporate Pt into a metal substrate, a metallorganic precursor, platinum(II) acetylacetonate [$Pt(C_5H_7O_2)_2$ or $Pt(acac)_2$], is selected as the precursor because it is less toxic and its thermal decomposition temperature is relatively low 210–240 °C [10]. The products of the thermochemical reaction [11,12] are Pt atoms and acetylacetone ($CH_3COCH_2COCH_3$). Pt is diffused into Ti and Ta substrates using the laser chemical vapor diffusion process. Ti and Ta are biocompatible materials with applications in medical treatments such as orthopedic and orthodontic applications. Often Ti plates and pins are used to repair fractured bones. Pt is also a biocompatible material. Tailoring the electromagnetic properties (e.g., transmittance) of Ti and Ta using Pt would enable nondestructive testing of these materials for detecting surface or internal defects when medical parts are produced using Ti or Ta. The electromagnetic response of these materials would also be useful for noninvasive medical examination of patients wearing implants made of these materials.

Each substrate was a 20 mm square sheet of thickness 25 or 50 μm. To avoid any bending or distortion of the sheets during laser heating, four edges of the substrate were clamped between two aluminum plates. Each plate had a square hole of side 18 mm. These two aluminum plates were placed on top of another aluminum plate without a hole. Therefore, only one side of the Ti and Ta sheets was accessible for laser heating and incorporation of Pt atoms. The clamped substrate was placed in a vacuum chamber as shown in Fig. 1 to carry out laser diffusion experiments. 200 mg of the Pt precursor was dissolved in 20 ml of acetylacetone and a bubbler was used to heat the solution with a hot plate by maintaining the temperature of the hot plate at 130 °C. The pressure of the vacuum chamber was lowered to about 10^{-3} Torr and the vapor of the precursor solution was then delivered to the chamber with argon gas until a total pressure of 2 atm was achieved inside the chamber. A Nd:YAG laser of wavelength 1064 nm was used for heating the substrate to cause thermal decomposition of the Pt precursor at the laser–substrate interaction zone and for diffusion of Pt atoms into the substrate.

The temperature of the substrate can be varied by changing various processing parameters such as the laser irradiance and scanning speed. The Ti substrates were irradiated with a laser beam of power $P_L = 12$ W for two scanning speeds $u = 6$ and 12 mm/s and two polarizations at each speed. The Ta substrates, however, required more energy to be sufficiently hot for the formation and diffusion of Pt into the substrate than in the case of the Ti sheets due to different thermophysical properties of these two metals. Therefore the Ta substrates were irradiated with a laser beam of power $P_L = 16$ W for two scanning speeds $u = 3$ and 6 mm/s and two polarizations at each speed. Thick samples require more energy than thin samples for the same increase in temperature and the reflectivity of rough surfaces is less than that

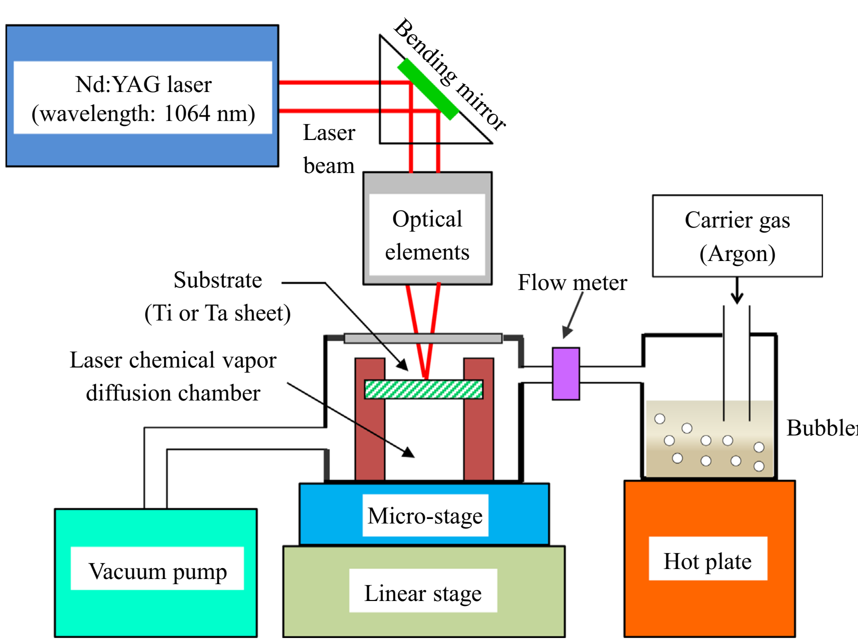

Fig. 1. Schematic of a laser chemical vapor diffusion system to incorporate diffusant atoms into substrates.