Effect of reactive atmosphere on pulsed laser deposition of hydroxyapatite thin films.

W. Mroz¹, M. Jedynski², J. Hoffman², M. Jelinek³, B. Major³, A. Prokopiuk¹, Z. Szymanski²

¹Institute of Optoelectronics of Military University of Technology, Kaliskiego St. 2, 00-908 Warsaw, Poland
²Institute of Fundamental Technological Research, Polish Academy of Sciences, Świętokrzyska St. 21, 00-049 Warsaw, Poland
³Institute of Metallurgy and Materials Sciences, Polish Academy of Sciences, Reymonta St. 25, 30-059 Cracow, Poland
⁴Institute of Physics, Academy of Sciences of Czech Republic, 18221 Prague 8, na Slovance 2, Czech Republic

E-mail : wmroz@wat.edu.pl

Abstract. Plasma plume induced by ArF excimer laser during the ablation of a hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) target is studied in different ambient conditions., i.e in air or water vapour. It is found that the plasma shape and plasma front velocities strongly depend on the ambient pressure. Appropriately selected reactive atmosphere enhances also the layer growth process.

1. Introduction

Pulsed laser deposition is a well-established method of deposition of thin films on different substrates. The particles ablated from a target owing to laser-target interaction form a plasma plume and subsequently are deposited on a substrate. The mechanism of plasma formation and expansion consists of three stages. During the interaction of the laser beam with a material the target is heated to the temperatures often exceeding the boiling temperatures and sometimes also the critical temperatures. Temperatures to which the target is heated depends on the mechanism of interaction of the laser beam with a material. When the absorbed laser energy is transformed into the heat then thermal ablation occurs. The second type of interaction called photochemical ablation takes place when the quantum energy of the laser radiation is high enough to break inter-atomic bonds and desorb particles from the surface [1]. This type of ablation is non-thermal and results in a much lower rise of target temperature. Usually both mechanisms are present. In the case of ArF laser with a wavelength 193 nm the energy of quanta is 6.3 eV and it can be assumed that the photochemical absorption is substantial. In the second stage the ablated particles are heated by the laser beam to the temperatures of some tens of kK and form a plasma plume. The characteristic time of plasma heating is 10-100 nanoseconds depending on the intensity of the laser beam and quantum energy [2]. Next the laser pulse terminates and plasma plume expands adiabatically. The expansion depends on the initial pressure of the plasma plume and the ambient pressure. The ablation rate also depends on the sort of the ambient gas and its pressure [3]. In this work plasma plume induced by ArF excimer laser during the ablation of a hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) target is studied in different ambient conditions., i.e. in air or water vapour. Hydroxyapatite is a biocompatible ceramic. It is deposited onto orthopedic implants in order to...
increase the bone-implant contact. It is found that the process of deposition significantly depends on the conditions of the plasma expansion.

2. Experiment and results

ArF laser operated at the wavelength of 193 nm with the pulse energy of ~300 mJ and 20 ns pulse duration. The emission spectra of the plasma plume were registered with the use of a 0.33 m focal length monochromator and a fast gate, micro-channel plate (MCP) image intensifier optically coupled to an Andor CCD camera. The image intensifier was gated by a high voltage pulse generator triggered by the signal from the laser. The same signal triggered the controller and started data acquisition.

The emission spectra consist mainly of calcium lines. The lines of other elements are weaker and overshadowed by calcium lines [4]. The electron density was determined from the Stark broadening of the 5188.84 Å Ca I line. In the case of the ambient pressure \( p = 0.008 \) Pa the electron density is \( \sim 3.5 \times 10^{23} \) m\(^{-3} \) near the target and drops to \( \sim 2.5 \times 10^{22} \) m\(^{-3} \) at the distance of 25 mm from the target. The accuracy is within ± 50%, which includes 25% accuracy of the experimental value of Stark broadening [5] and the experimental error. The electron temperature was determined from the ratios of intensities of the 3933.66 and 3706.02 Å Ca II ionic lines and the 5512.98, 5041.62, 6717.68 Å Ca I atomic lines, as well as from relative intensities of 5512.98, 5041.62, 6717.68 Å atomic lines. The transition probabilities were taken from [6]. Due to the relatively high electron density, \( N_e \gtrsim 1022 \) m\(^{-3} \), it can be assumed that the laser induced plasma is in the local thermal equilibrium (LTE). It was estimated that the transport of particles did not influence LTE. The lines used for the temperature and electron density determination are free from the self-absorption, at least close to the target (atomic lines) and far from it (atomic and ionic lines). In the case of the pressure \( p = 10 \) Pa the temperatures of 6.5-3.5 kK are found at distances of 19-29 mm from the target, respectively. The accuracy is about ± 50%. The above values are obtained from the line profiles and intensities integrated over the time and the plasma depth seen by the detector. Near the target, electron temperature was estimated from the evaluated pressure and electron density. Assuming that the plasma is practically fully ionized the temperature about 30 kK is found. The pressure of the plasma plume was estimated assuming that 50% of laser energy is converted into ablation of particles. The binding energy of hydroxyapatite is 12.75 eV per atom [7]. Then 150 mJ produces \( \sim 0.73 \times 10^{17} \) atoms and 22.7% of them, that is \( 1.65 \times 10^{16} \), are calcium atoms. After 50 ns from the laser pulse the plasma shape is nearly spherical with the radius of \( \sim 0.15 \) cm (does not depend on the pressure). This gives total particle density of \( 4.8 \times 10^{18} \) and the total pressure of \( 13 \times 10^5 \) Pa, and in turn \( 2.9 \times 10^5 \) Pa of calcium partial pressure.

The dynamics of plasma plume was recorded by means of fast photography. High-voltage pulse gated the image intensifier for 18 ns while the delay time between the laser pulse and HV pulse was changed gradually from 50 ns to 3 μs. The monochromator was removed and the 4226.7 Å Ca I and 3933.6/3968.4 Å Ca II lines were separated with the use of Melles-Griot interference filters together with proper cut-off filters. It was found that Ca I line and Ca II line radiate from the same place; there was no significant differences in the location of the neutral and singly ionized atoms during plasma expansion. Figure 1 clearly shows the influence of the ambient pressure on the shape of the plasma plume. In the case of the higher ambient pressure the plasma is compressed by the ambient gas. The results presented in figure 2 show the velocities of the luminous plasma front in the direction perpendicular to the target. Although the accuracy of the experimental points at distances lower than 1 cm is poor the general tendency is clear. The plasma velocity is constant during the expansion into vacuum and decreases when the ambient pressure is few Pascals.

In the case of HA layer deposition, an appropriately selected reactive atmosphere enhances the layer growth process. Figure 3 shows the topographies of two HA layers deposited in the atmosphere of water vapour at the pressure of 35 Pa (in this case \( p_{eff} = 0.5 \times \text{pressure reading} \)) and in the residual air pressure of 0.01 Pa. The results with air at \( p = 0.35 \) Pa are similar to that with water vapour.
Figure 1. Plasma images at two different pressures of the ambient gas: upper images $p=0.01$ Pa, lower $p=10$ Pa. Radiation of the 4226.7 Å Ca I line. Delay from the laser pulse 50, 800, 1500 ns, respectively.

Figure 2. Velocities of the luminous front of the excited Ca atoms (4226.7 Å) in the direction perpendicular to the target in different ambient conditions.

The phase analysis made with diffractometer (XRD) showed that the reduction of water vapour and decrease of the pressure in the experimental chamber results in the decay of the crystalline structure characteristic for HA. Structural analysis of the layers deposited in the atmosphere of water vapour and in vacuum, made with Fourier transform infrared spectrometer (FTIR) in the range between 400 and 4000 cm$^{-1}$, indicated changes of the measured spectrum only within the range of 950 -1100 cm$^{-1}$. Thus, the layers deposited in vacuum remain hydroxyapatite layers, in spite of their amorphous structure. Similar investigations were presented in [8].
3. Summary

The plasma plume induced by ArF excimer laser ablation of a hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) target was studied in different ambient conditions. The electron densities between 3x10²³ + 3x10²² m⁻³ are found depending on the distance from the target. The temperatures fall to 6.5 ± 3.5 kK at the distances 19-29 mm from the target. Plasma velocities are of the order of 10⁴ m/s and generally they decrease with the distance from the target. However, when plasma expands into vacuum then the velocity increase with the distance from the target. The ambient pressure also influences the shape of the plasma plume. In the case of the higher ambient pressure the plasma is compressed by the ambient gas. Appropriately selected reactive atmosphere enhances the growth of the deposited layer.

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