Time resolved emission spectroscopy investigations of pulsed laser ablated plasmas of ZrO$_2$ and Al$_2$O$_3$

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**Abstract.** With the rising trend of synthesizing ultra thin films and/or quantum-confined materials using laser ablation, optimization of deposition parameters plays an essential role in obtaining desired film characteristics. This paper presents the initial step of plasma optimization study by examining temporal distribution of the plasma formation by pulsed laser ablation of materials. The emitted spectra of ZrO$_2$ and Al$_2$O$_3$ are obtained ~3mm above the ablated target to derive the ablated plasma characteristics. The plasma temperature is estimated to be at around 2.35 eV, with electron density of 1.14x10$^{16}$ (cm$^{-3}$). Emission spectra with different gate delay time (40-270 ns) are captured to study the time resolved plume characteristics. Transitory elemental species are identified.

1. Introduction

Pulsed Laser Deposition (PLD) has gained much attention, because they have important applications in materials processing and thin film deposition [1]. Several of the main advantages for PLD techniques are: capability for stoichiometric transfer of material from target to substrate, very high efficiency (deposition rate), reduced chamber size and capability of depositing composite film with multiple targets [2, 3]. The vaporized material, containing neutrals, ions, electrons etc., quickly form laser-produced plasma and expands rapidly away from the target surface (with velocities typically ~10$^6$ cms$^{-1}$ in vacuum). Incorporation of background gas will change the nature of plasma expansion, involving background gas compression and collision between ejected constituents and background gas, creating more confined plasma promoting the nucleation and condensation of particulates.

The characteristics of synthesized particles largely dependent on a number of parameters, especially the fabrication conditions (target-substrate distance, ambient gas, and pressure) and initial plasma forming conditions (laser wavelength, pulse width, laser energy, repetition rate). The initial conditions determine how materials are ejected (size, phase: vapor, liquid, solid) from the targets. On the other hand, the plasma expansion and material transport are controlled by the fabrication conditions, especially presence of ambient gas and pressure. Thus, to optimize the synthesis of film deposition by laser ablation, it is relevant to study several aspects of plasma formation: the initial plasma forming condition, plasma expansion, and transportation of materials from target to the substrate end.
ZrO$_2$ has been identified as one of the potential high-k dielectric replacement for SiO$_2$ [3-6]. Unfortunately, some problem with ZrO$_2$-Si interface has been found, forming silicate [7] layer and silicide islands [8] during later stages of annealing at high temperatures. An intentional buffer layer of Al$_2$O$_3$ is proposed to address the interfacial issue, and in the same time increases the total capacitance in the newly proposed stacked dielectric layer. Compared to atomic layer deposition (ALD) and chemical vapor deposition (CVD), which requires complex different precursors (and also chances of contamination problems); PLD simplifies the method, enabling the usage of two different targets to build composite or layered structure on top of silicon substrate. In this paper, we report a study of ZrO$_2$ and Al$_2$O$_3$ laser ablation in vacuum, focusing on initial plasma forming condition.

2. Experimental Details

A Continuum Surelite Nd:YAG laser of 1064 nm was used in this experiment, with constant pulse energy of 68 mJ, ~17 ns pulse duration at 1.1 kV operating voltage. The laser was focused using spherical lens to a spot size of ~50 µm. The laser radiation falls normal to target side surface. The targets used in the entire experiments are in rod form of purity ~99.99% with ~1 inch base diameter and ~2.5 cm height. The target rod was continuously rotated and at the same time translated in Z-axis by a fully computerized motor, such that laser radiation falls to a fresh surface each time. Vacuum chamber is flushed down to ~10$^{-5}$ Pa before laser is shot. Optical spectroscopy method is used in present work, utilizing light monochromator and gated ICCC camera. Plasma was imaged onto a slit of Acton® 750 optical monochromator with a lens focusing at a position about 3mm above the target rod. The output of monochromator was detected with gated (synchronized with laser trigger) ICCC camera with suitable gate delays to obtain time resolved spectrum.

The ZrO$_2$-Al$_2$O$_3$ bi-layer is deposited on silicon substrate at room temperature, by ablating first the Al$_2$O$_3$ target rod, followed by ZrO$_2$ rod ablation in vacuum of ~10$^{-5}$ Pa. Transitory elemental species were identified by matching the lines with NIST Database [9]. Electron density is estimated using Stark broadening, and the electron temperature is derived from the spectra intensity data of O II ionized species. The dynamic nature of the plume is studied by observing the intensity pattern changes of different gate delays, ranging from 40 – 270 ns. The temporal variation of the ablation plume was studied by capturing the spectra at different gate delays, at a constant width of either 10 or 40 ns.

3. Results and Discussion

3.1. Plasma emission identification

Figures 1 (a and b) show the typically identified ZrO$_2$ plasma lines at 403 and 613.5 nm center wavelength respectively. Subsequently, figs. 2 (a and b) show the typically identified plasma lines of Al$_2$O$_3$ at 396 and 466 nm center wavelength. The spectral lines were captured as images in “raw” format from ICCD using a Linux based sgrab software via a frame grabber card. The raw images were then processed using ImageJ freeware to plot the relative intensity of different spectral lines with respect to the background signal. Observations were done on more than one spectral window to accommodate the estimation effort of electron temperature and density.

The observed lines were fairly distinct with some broadening in several places. There are several reasons for this, including merging of several lines in close proximity, resolution limit of the spectrometer, and also broadening mechanisms due to species interactions, which will be useful to predict the plasma density. Difficulties were faced during Al$_2$O$_3$ plasma observation, mainly due to faint and blurry lines, later known that Oxygen lines (with much lesser intensity) dominate especially on the visible range. Target rod contamination was detected, by the appearance of Zr I line at 468.342 (see fig. 2(b)). This is suspected due to target handling.
3.2. Time Resolved Spectroscopy
The temporal evolution of ZrO$_2$ plasma at 613.5 nm centre wavelength (40 ns width) at variable gate delays was captured (not shown). The spectral width (and thus density) decreases as time progresses. Fig. 3 shows the shifting trend of Oxygen II lines at 613.375 nm towards the longer wavelength. This could be attributed to the dynamical change of density and temperature of plasma with time, as proposed by Narayanan and Thareja [10].
Figure 3: Peak shifting phenomena of Zr I at 613.455 (original) towards the lower wavelength.

A similar temporal evolution was observed for Al2O3 spectra, with notably lower peak intensity (not shown), which is expected since Al2O3 possesses significantly lower atomic mass than ZrO2. The intensity of all lines were increasing during the time from 90-140ns before it abruptly becomes a continuum at >150 ns delay. Observation of plasma spatial and temporal evolution is useful as a powerful guide to obtain the plasma parameter at certain distances (and pressure), thus further spatial study of the plasma will come handy to determine optimum parameter for deposition purposes.

3.3. Electron Temperature Measurement

Hafez et al. [11] and similarly Ismail et al. [12] proposed a way to measure the electron temperature by using the relative densities of few lines, by utilizing the Boltzmann’s relation:

$$I_{mn} = \frac{\hbar c}{4\pi} \frac{g_m A_{mn}}{\lambda_{mn}} \frac{N(T)}{U(T)} \exp \left( -\frac{E_m}{kT_e} \right)$$  \hspace{1cm} \text{Eq. 1}

Where $I_{mn}$, $g_m$, $A_{mn}$, $\lambda$, $N(T)$, $U(T)$, $E_m$, and $T_e$ are the intensity, statistical weight, transition probabilities, wavelength, total density of ions, partition function, energy level and electron temperature respectively. The subscript $m$ denotes the higher excitation state, refers to $k$ (and similarly $n$ to $i$) as described by Martin & Wiese [13] and NIST resources [9].

Rearranging equation 1, we get:

$$\ln \left( \frac{I_{mn} \lambda_{mn}}{g_m A_{mn}} \right) = \ln \left( \frac{N(T)}{U(T)} \right) - \frac{E_m}{kT_e}$$  \hspace{1cm} \text{Eq. 2}

$\ln(I/gA)$ vs. $E_m$ plot was used to deduce the electron temperature $T_e$ by calculating the linearized slope. In our case, O II lines at several chosen wavelengths were used to estimate ZrO2 plasma temperature; while O I lines were used for Al2O3 plasma. Iterating the calculation over different gate delays for both plasmas, we obtained the time evolution characteristics of the plasma temperature. The detail iteration results are not shown in the paper due to space constraint.

Figure 4: Temperature distribution over time of (a) Al2O3 (b) ZrO2. Solid line is Gaussian fit.
The temperature distributions were found to be in the range of ~5 eV for ZrO$_2$ plasma and ~2-4 eV for Al$_2$O$_3$ (see fig. 4(a,b)). According to the Gaussian fit of ZrO$_2$ temperature trend over time, peak temperature happens at around 45 ns, spanning across 15 ns width. Al$_2$O$_3$ plasma reached its peak temperature at 190 ns with half span of almost 100 ns. This may give some rough idea about the plasma lifetime, how fast is the laser-target and laser-plasma interaction. The temperature obtained in this experiment is the temperature of the plasma 3 mm away from the target, close to hottest region of the plasma (about 2 mm above target [10]).

4. Conclusions

We have characterized the laser ablated ZrO$_2$ and Al$_2$O$_3$ plasma in vacuum. Plasma emission lines were captured and temporal species were identified with aid of NIST Spectral Lines Database [9]. Temporal evolution of both plasmas was studied. The spectral width and intensity decreases as a function of time. It was observed that the captured intensity drops ~50-130 ns after the first few sightings of continuous spectra bands. From the time resolved spectroscopy, ZrO$_2$ plasma lifetime is estimated to be around 200 ns, while Al$_2$O$_3$ has shorter lifetime of around 50 ns. Electron temperature distribution over time of both plasmas was estimated. It was found that the temperature fluctuates during the formation of the plume, ranging from 5.4 to 5.9 eV for ZrO$_2$ plume, and 1.75 to 4.25 eV for Al$_2$O$_3$ plume. Gaussian fit of both temperature trend plots gives an estimation of how the transient plasma evolves with time.

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