Pulsed laser deposition with a high average power free electron laser: Benefits of subpicosecond pulses with high repetition rate

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We have conducted experiments exploring pulsed laser deposition of thin films using the high average power Thomas Jefferson National Accelerator Facility Free Electron Laser. The combination of parameters of this laser, including subpicosecond pulses, high average power, high repetition rate, and tunability, makes it a unique tool for the study of the effects of laser characteristics on thin-film quality. When compared to ablation and deposition with an ultrafast, high energy per pulse, low repetition rate laser (amplified Ti:sapphire), we find that the lower energy per pulse with high repetition rate of the free electron laser leads to very different plasma emission and produces films with high quality with the potential of very high deposition rates. This is demonstrated in the optical spectroscopy of plasma emission from Ti and the growth of $Ni_{80}Fe_{20}$ thin films. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1543646]

I. INTRODUCTION

Pulsed laser deposition (PLD), the technique by which material is ablated from a target by interaction with a high fluence, pulsed laser beam and deposited onto a substrate, is an extremely versatile and powerful film growth technique.[1] Nanosecond pulsed lasers, particularly excimers, are currently the standard used in PLD, but recent work has explored the benefits of using other systems, particularly ultrafast lasers and also high repetition rate lasers. Ultrafast (pulse widths <10 ps) lasers have shown dramatic benefits[2] in less target damage, lower ablation thresholds, elimination of the particulate problem, and the creation of unique ablation conditions such as a highly ionized plasma.[3] Amplified picosecond and femtosecond laser sources, however, are typically limited in repetition rate to tens of Hz to kHz. Exploration of PLD with lower energy per pulse but higher repetition rate lasers has shown advantages of higher quality films with high deposition rates.[4] Although there has been an increasing number of laser sources introduced into PLD, it is beneficial to continue to explore a wider range of laser parameters (pulse widths, tunability, repetition rate) to enhance the capabilities of PLD.

The high average power Thomas Jefferson National Accelerator Facility Free Electron Laser (TJNAF-FEL) in Newport News, VA, commissioned in 1999, presents a unique opportunity in a *combination* of parameters unavailable to other laser systems. Specifically, we can study the combined effects of short pulses (<1 ps), high average power (>2 kW), high and varying repetition rate (18.7, 37.4, or 74.8 MHz) and wavelength tunability (currently in the IR). Unlike other FELs, the TJNAF-FEL can be run in both pulsed mode (with macropulses in the μs to ms ranges) at repetition rates up to 1 kHz, as well as in cw mode (with a continuous train of micropulses at 18.7, 37.4, or 74.8 MHz). A major strength recently demonstrated of using a free electron laser in PLD is its tunability. This was shown in the resonantly enhanced deposition of polymer thin films with preserved character.[5] With the TJNAF-FEL, the combination of high average power and high repetition rate makes it possible to reach fluences necessary for routine deposition of a wide range of materials and the exploration of a variety of parameters on the thin-film quality.

In this article we report deposition experiments conducted with the TJNAF-FEL. When compared to ablation and deposition with an ultrafast, high pulse energy, low repetition rate laser (amplified Ti:sapphire), we find that the lower pulse energy with very high repetition rate of the free electron laser leads to very different plasma emission and produces films with markedly different quality at very high deposition rates.

II. EXPERIMENTAL SETUP

In this work, optical emission spectroscopy of the ablated plasma plume of Ti and deposition of $Ni_{80}Fe_{20}$ (permalloy) were carried out with the TJNAF-FEL (650 fs pulse widths at a 18.7, 37.4, or 74.8 MHz micropulse repetition rate) and an amplified Ti:sapphire system (Spectra-Physics Tsunami and Spitfire system with ~150 fs pulse widths at a 1 kHz repetition rate). For these experiments, the FEL had a wavelength ranging from 2.9 to 3.1 μm and pulse energies of 5 to 20 μJ were used. The amplified Ti:sapphire wavelength was 800 nm and pulse energy was 0.5–0.7 mJ. Ablation and deposition were studied in an 8 in. turbopumped vacuum chamber with a pressure of $\sim 1\times 10^{-6}$ Torr. A schematic of the setup for is shown in Fig. 1. Laser input and viewing windows were made of sapphire. The targets used were 99.99% pure metal targets purchased from Angstrom Scientific Inc. and were rotated by a dc motor (~1 revolution/s).

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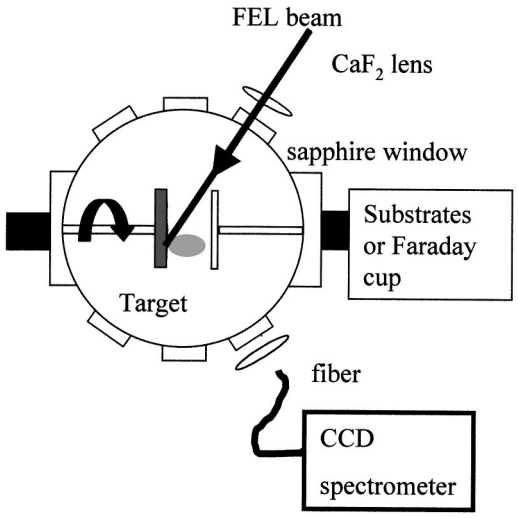

FIG. 1. Schematic of PLD vacuum chamber used in experiments at the TJNAF-FEL and with the amplified Ti:sapphire system.

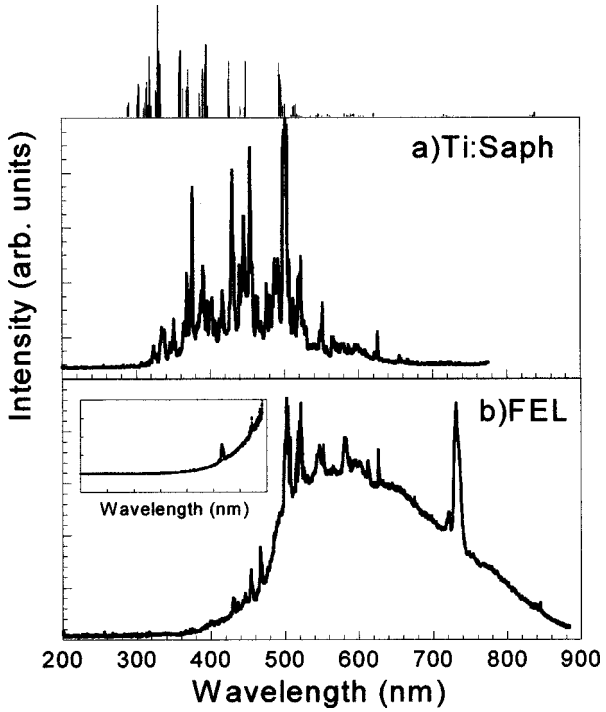

FIG. 2. Optical spectra recorded from ablation of Ti with (a) an amplified Ti:sapphire laser at 0.5 mJ/pulse at 1 kHz and (b) the TJNAF-FEL at 20 μJ/pulse, 18.7 MHz, 200 μs macropulses at 60 Hz. For the FEL spectrum, lines at 731, 580, and 516 nm are harmonics of the FEL beam. Inset: spectra corrected for spectrometer response, with fit for blackbody emission. The lines at the top of the figure are the lines for Ti emission taken from the NIST database.

Silicon substrates were used for the $Ni_{80}Fe_{20}$ deposition and were mounted to an aluminum plate (with neither heater nor cooling provided). The target–substrate distance was 2 in. The substrates were cleaned in acetone and alcohol before placement in the chamber. Characterization of the ablation was carried out by means of optical spectroscopy of the plasma emission with a fiber-coupled charge-coupled-device (CCD) spectrometer (Ocean Optics) with 1 nm resolution. The emission was focused with a fused silica lens onto the fiber input. Other characterization included time-resolved optical emission by a Hamamatsu photomultipler with input into a fast Tektronix scope and a Faraday cup for time-resolved measurements of electron and ion output.

For experiments with the TJNAF-FEL, the chamber setup shown in Fig. 1 was placed on an optical table in the beamline of the FEL. The FEL beam was focused onto the target with either a 25 or 50 cm CaF_2 lens, placed on a translation stage so the best focus could be achieved. This gave approximate spot sizes of $\sim$100 and 200 μm, respectively. The deposition rates with the FEL were so high that the input window was quickly coated with material, which led to distortion and absorption of the beam (and ultimate destruction of the window). To circumvent this problem, a window assembly (PVD Products), with a rotating sapphire plate to catch the deposited material, was used during thin-film growth. For ablation and deposition with the amplified Ti:sapphire laser, a 25 cm focusing lens was used, with focus spot sizes of $\sim$100 μm.

The thin films produced in this work were analyzed structurally by scanning electron microscopy, atomic force microscopy (CP Research) and x-ray diffraction using a Cu $K\alpha$ source (Phillips). A profilometer (Dektak) was used to measure the film thickness. The magnetic properties of the NiFe films were measured with a vibrating sample magnetometer (VSM Lakeshore) with a magnetic field applied parallel to the sample plane.

III. EXPERIMENTAL RESULTS

A. Characterization of plasma plume

The emission spectra of the plasma plumes for ablation of a Ti target with an amplified Ti:sapphire laser and the TJNAF-FEL are shown in Fig. 2. For Fig. 2, the FEL was running in macropulse mode with 1 ms pulses at 60 Hz (with a 18.7 MHz micropulse repetition rate). The spectra uncorrected for spectrometer (grating) response are shown for emphasis. For the amplified Ti:sapphire system, the plume gave significant neutral and ion emission. To the eye, the plumes were blue in color. In contrast, the emission from FEL ablation showed overwhelming blackbody radiation. To the eye, the plumes were dense and white. With the spectrometer, individual emission lines were seen, but were overwhelmed by the blackbody emission. As the repetition rate, macropulse length, or power were increased, the amount of blackbody radiation overwhelmed the single line emission. To confirm that this is blackbody emission, the inset in Fig. 2(b) shows the spectra corrected for spectrometer response along with a curve for blackbody emission at 2400 K. With the FEL in macropulsed mode, changing the repetition rate or average power changed the intensity of emission but did not change the temperature of the plume extracted from the spectra. When the laser was run in cw mode (with the same pulse energy and repetition rate), the temperature decreased to 1700 K. Spectra of FEL ablation plumes for other materials were also measured and all showed a large amount of blackbody radiation. The spectra shown were taken with the fiber

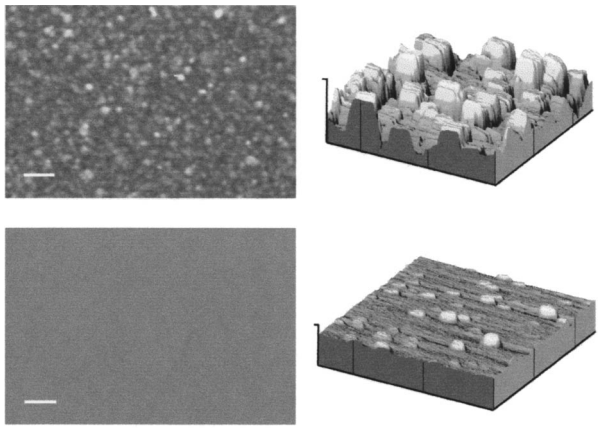

FIG. 3. SEM (left) and AFM (right) scans for thin films grown with (a) the amplified Ti:sapphire system (top pictures) and (b) the TJNAF-FEL (bottom pictures). For the SEM scans, magnification ~13 000× (the white line indicates 1 μm). For the AFM scans, dimensions are 5 μm square and the line indicates 1500 Å height.

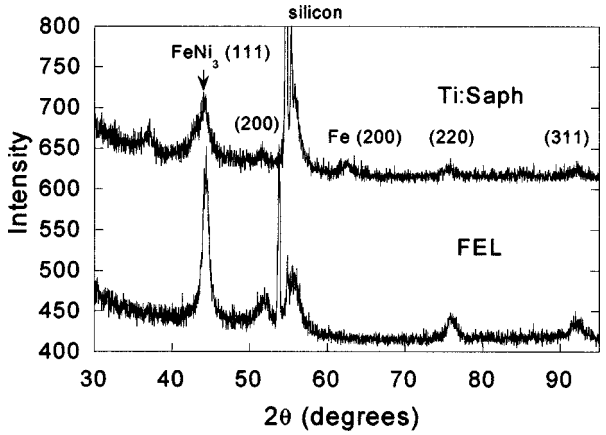

FIG. 4. XRD spectra for films grown with amplified Ti:sapphire (top) and FEL (bottom).

viewing the target, but it should be noted that the blackbody spectra were also observed when the spectrometer was viewing the plasma from the side. We have performed some initial time-resolved optical emission experiments and have found that the emission does show enhancement with each individual micropulse.

Preliminary results with the Faraday cup reveal a significant emission of electrons and ions during the ablation process. For time-resolved measurements, the same micropulse structure as seen for the optical emission is seen for the electron/ion emission, confirming again that individual micropulses are contributing to the ablation process. We were unable to resolve the energies of the electrons and ions with our equipment, but can only set an upper limit of 100 eV at the substrate distance of 2 in.

B. Thin-film quality

To test thin-film quality, we compared NiFe (permalloy) films grown with FEL PLD and amplified Ti:sapphire. This material was chosen for its importance as a magnetic metal and its sensitivity to deposition conditions. We have also produced thin films of other materials. We have found that the best films are produced for cw mode and at higher repetition rates. It is believed that having the target and plume continuously bombarded with pulses aids in the deposition process. Comparison with films grown with the amplified Ti:sapphire gives a good illustration for this. The general character of the films is shown in the scanning electron microscopy (SEM) and atomic force microscopy (AFM) scans of the films of Fig. 3. For the films shown, the amplified Ti:sapphire had pulse energy of 0.7 mJ while the FEL was running in cw mode at 37.4 MHz with a pulse energy of 5 μJ. The films grown with the low repetition rate amp:Ti:sapphire laser are granular (the film had a granular appearance to the eye) with nanometer-sized particles. The film shown below had an average (rms) roughness of 275 Å. The FEL film is smooth in comparison, with an average roughness of 44 Å. Figure 4 shows the x-ray diffraction (XRD) spectra, and the higher quality of the FEL film is shown in the narrower, stronger (111) $FeNi_3$ peak. The amp:Ti:sapphire grown film shows a small amount of crystallized Fe. The film quality has obvious effects on the magnetization, as shown in Fig. 5. The amp:Ti-sapphire film is highly coercive (coercivity 115 G) while the coercivity of the FEL film is very low (2 G). The larger coercivity of the Ti:sapphire grown film could be due to a combination of the crystallized Fe phase, less crystalline orientation, and rougher surface.

The most dramatic difference in PLD with these two laser systems is in the deposition rates. For the Ti:sapphire film, ~1400 Å of material was deposited in ~20 min, with a deposition rate of ~1 Å/s or 1×10^{-3} Å/pulse. For the FEL, a ~1000 Å film was grown in ~1 min, with a deposition rate of ~17 Å/s or 5×10^{-7} Å/pulse. Even higher deposition rates are expected with the TJNAF-FEL for higher fluences, higher repetition rates, and different focusing and vacuum conditions (a rate of 200 Å/s was recently measured for Nb film deposition[6]).

IV. DISCUSSION

From the optical spectra and quality of thin films, it is clear that the character of the ablation and deposition is very different for the cases of an ultrafast, high energy per pulse, low repetition rate laser versus and ultrafast, low energy per

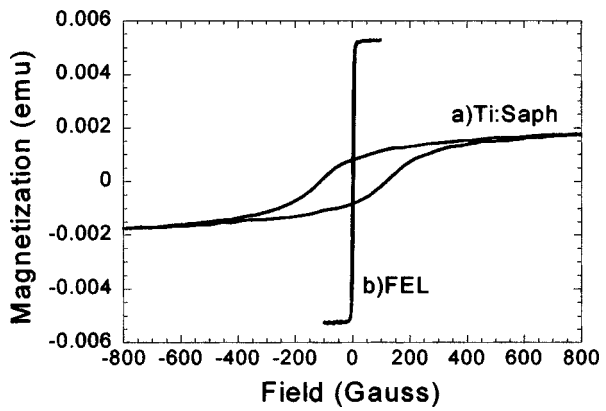

FIG. 5. Magnetization curves for NiFe films produced with the (a) amplified Ti:sapphire system and (b) the FEL.

pulse, high repetition rate laser. Better film quality (as measured by crystalline structure, film smoothness, and magnetic properties) is achieved by having lower energy per pulse but higher repetition rate. This has also been demonstrated by PLD of carbon[4] by Gamaly and co-workers. They believe that this is due to the fact that for high repetition rate there is continuous vapor flow, with slower atoms from the previous pulse mixing with faster atoms from the subsequent pulse. For the case with the FEL, the dense, white plasma may also indicate that the ablated species are undergoing many interactions (scattering events) with each other, which may also aid in improving film quality. Thus, the significant blackbody radiation may be characteristic of a dense, highly interacting plasma which is continually being fed by high repetition rate pulses. Such a high-density effect has been seen in pulsed laser ablation with a nanosecond UV source, but only near the target surface.[7] The second possibility to explain the blackbody emission is that it is coming from heated nanoparticles in the plume.[8]

One point of interest regarding the growth of magnetic thin films is how sensitive the coercivity is to the laser parameters. This illustrates the great flexibility PLD gives in producing magnetic thin films of varied properties and may be useful in depositing multilayers where varying coercivities are needed (such as in giant magnetoresistive multilayers).

V. CONCLUSION

This work has demonstrated additional possibilities of using a high average power free electron laser for the study of pulsed laser deposition. FEL-PLD is capable of producing high quality films with very high deposition rates and offers the opportunity to study the effects of a wide range of parameters on thin-film quality.

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