Pulsed laser ignition of reactive multilayer films

Yoosuf N. Picard[a)]
Department of Materials Science and Engineering, University of Michigan, 2300 Hayward Street, Ann Arbor, Michigan 48109-2136

David P. Adams and Jeremy A. Palmer
Sandia National Laboratories, P.O. Box 5800, Albuquerque, New Mexico 87185

Steven M. Yalisove
Department of Materials Science and Engineering, University of Michigan, 2300 Hayward Street, Ann Arbor, Michigan 48109-2136

Nanostructured Al/Pt multilayer films were ignited by single pulse irradiation from a Ti:sapphire femtosecond laser system. Critical ignition fluences ($0.9-22$ J/cm^2) required to initiate a self-propagating reaction were quantified for different multilayer designs. Multilayers with smaller bilayer thickness required relatively lower fluence for ignition. Ignition threshold fluence was also found to be 1.4–3.6 times higher for Al-capped multilayers than for Pt-capped multilayers. Ablation threshold fluences were measured for Al (860 ± 70 mJ/cm^2) and Pt (540 ± 50 mJ/cm^2) and related to the observed difference in ignition fluences for Al- and Pt-capped multilayers. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2191952]

Reactive multilayers are nanostructured materials that provide an approach to self-propagating high temperature synthesis (SHS) of new alloys and show potential for use in alternative joining processes. These nanolaminates consist of alternating layers of reactants having a large negative enthalpy of mixing. Upon local ignition from an external energy source a portion of the layers interdiffuses, resulting in a rapid exothermic reaction. The heat generated can initiate further mixing and self-propagate the reaction through the entire film. Self-propagating reactions have been reported since the 1950s (Ref. 1) for powder mixtures and were later first demonstrated in vapor-deposited multilayer thin films.[2] A large number of exothermic thin film systems that exhibit SHS reactions have since been reported, including Ni/Al,[3] Nb/Si,[4] and Ti/Al.[5] Recent interest in reactive multilayers stems from their potential use as a local heat source for soldering[6] and brazing[7] applications.

Recent work igniting energetic powder mixtures has employed lasers as a means for determining ignition temperatures and energies.[8–10] Lasers provide a controllable source of energy that can be used to better quantify ignition parameters still unknown for many reactive material systems. Short-pulsed lasers, in particular, allow for controlled energy deposition into a small volume. It has been shown that femtosecond pulse lasers can be used for machining of explosive materials without ignition due to highly limited energy dissipation.[11] Similarly, femtosecond pulse length lasers can controllably machine reactive multilayers without ignition, first demonstrated for Ni/Al (Ref. 12) and Co/Al (Ref. 13) multilayers.

In this study, Al/Pt multilayers were discovered to ignite upon single pulse exposure from a femtosecond laser. The Al–Pt pair is highly energetic, characterized by a large heat of formation [-100 kJ/mol of atom s at 25 °C (Ref. 14) for a 1:1 stoichiometry]. For this work, we measured ignition thresholds by irradiating multilayer Al/Pt films on substrates

with single pulses from a femtosecond laser with increasing energy until a self-propagating reaction was observed. We relate the measured ignition fluence threshold to the bilayer thickness of the multilayer system and the identity of the metal capping layer.

Al/Pt films were comprised of alternating stacks of Al and Pt layers with an Al to Pt thickness ratio of roughly 10:9 in order to obtain a 1:1 atomic ratio.[15] The Al/Pt films were deposited using planar magnetron sputtering with an Ar back pressure of 10 mTorr onto 2 cm square pieces of Si (100) wafers with a 400 nm thick thermally grown oxide. A thick, fully dense SiO$_2$ layer is chosen so as to prevent Si intermixing with Al and Pt during SHS. All films for ignition studies were roughly 1.6 μm in total thickness but with different Al/Pt bilayer thicknesses (defined as the combined thicknesses of single Al and Pt layers) ranging from 325 to 975 Å.[16] Figure 1 presents an image of a typical Al/Pt reactive multilayer prior to ignition.

All laser irradiation studies were carried out in air with films attached to substrates and maintained at 25 °C prior to ignition. A Ti:sapphire laser system produced 120 fs pulses, at 800 nm wavelength with a 1 kHz repetition rate. Individual pulses were directed through a 20× objective lens and
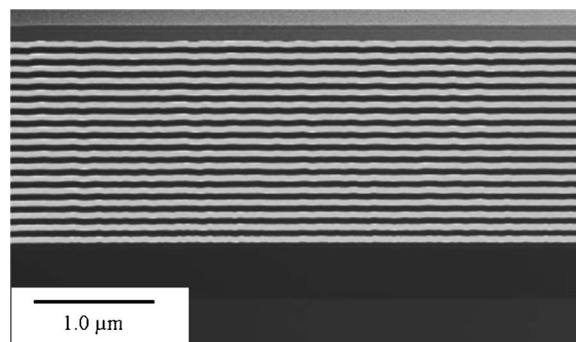

FIG. 1. (Color online) Transmission electron micrograph of 17 bilayer Al/Pt reactive multilayer with 975 Å bilayer thickness.
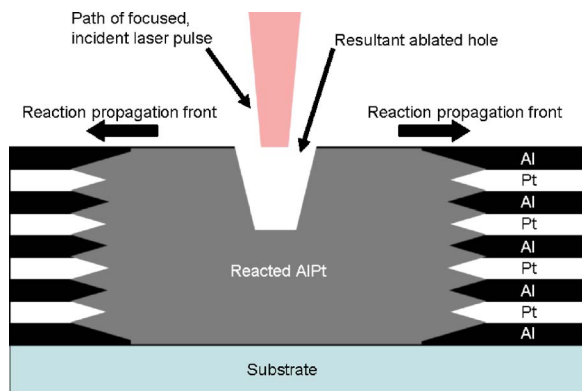
a)Electronic mail: ypicard@umich.edu

FIG. 2. (Color online) Schematic of laser ignition process for an Al-capped Al/Pt reactive multilayer. Following irradiation of a single pulse of sufficient energy for ignition, a zone of intermixing or reaction front propagates radially away from the irradiation region until the entire multilayer is reacted.

focused onto the sample surface to a roughly 8 μm diameter spot size ($1/e^2$ Gaussian energy distribution). The sample was positioned using a two-axis stage with 2 μm accuracy. For each sample, a series of single pulses with incrementally increasing energy was applied near the center of the sample until ignition was observed. The single pulse exposures were spaced significantly (200 μm) apart to minimize any heating affects from subignition threshold laser irradiation. Ignition was characterized by a visible flash across the entire sample surface as well as a substantial increase in film roughness. A schematic of the laser ignition process is presented in Fig. 2.

Figure 3 plots femtosecond laser ignition fluence threshold to ignite a self-propagating reaction versus the bilayer thickness for different Al/Pt multilayer films. The ignition threshold increases with increasing bilayer thickness. All measured ignition thresholds (0.9–22 J/cm^2) are above typical ablation thresholds for metals under femtosecond laser irradiation.[17] Hence, material ablation, or removal, occurs in addition to ignition of a self-propagating reaction. Studies involving femtosecond laser ablation of metals have observed two ablation regimes depending on laser fluence.[18] In the low ablation fluence regime, heat sufficient to remove material is mostly confined within the optical penetration depth. In the higher ablation fluence regime, significant thermal energy dissipates outside the optical penetration depth,
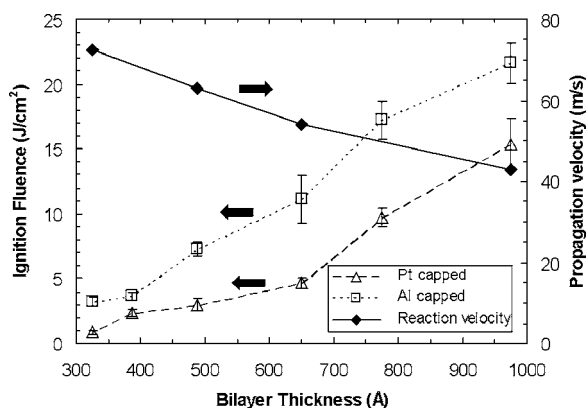

FIG. 3. (Color online) Femtosecond laser ignition fluence and reaction propagation velocity plotted vs bilayer thickness for Al/Pt reactive multilayers. Ignition fluences for both Pt- and Al-capped multilayers are presented.

causing further evaporation and melting. For the latter regime, extent of material modification is related to a thermal diffusion length (2–20 times longer than the optical penetration depth[19,20]) where heat conduction is paramount. Recent studies have helped to confirm the increase in heat affected zone (HAZ) widths across these regimes.[21] The transition fluence between these two regimes is roughly 0.6–3 J/cm^2 for various metals.[17–21] All ignition thresholds measured in this work fall within the high fluence ablation regime, with implications that energy dissipation exceeds the optical penetration depth [calculated[22] as 74 Å for Al and 130 Å for Pt (Ref. 23)]. We surmise that fluences necessary for ignition lead to material removal combined with heat diffusion into the multilayer sufficient to cause multiple layer intermixing.

It has been shown that the steady-state propagation velocity of reactive multilayers depends on bilayer thickness.[24] Propagation of the reaction front is mass-transport limited, and therefore the propagation velocity is strongly dependent on the length of atomic diffusion necessary for intermixing. This atomic diffusion length is on the order of the bilayer thickness for a given design. For thinner bilayers, the propagation velocity is increased as the atomic diffusion length is correspondingly smaller. This relationship between the propagation velocity and the bilayer thickness for the Al/Pt multilayer designs is plotted in a portion of Fig. 3. Velocities were measured using high-speed photography for four Al/Pt multilayer films described elsewhere.[25]

From Fig. 3, it is evident that the ignition fluence and reaction propagation velocity are both dependent on bilayer thickness. With increasing fluence, the HAZ is larger and penetrates deeper into the target material. This premise has implications regarding laser ignition phenomenon. For thinner bilayer thickness, the time necessary for requisite mixing is less and should result in more rapid release of heat, requiring a smaller HAZ. Films of thicker bilayer design require a larger HAZ to mix sufficient amounts of Al and Pt in order to stimulate ignition of a self-propagating reaction. Therefore, we believe laser ignition is affected by both thermal and mass transport similarly to propagation velocity.

It should be noted that a premixed 100 Å thick amorphous AlPt layer is present at all layer interfaces prior to laser irradiation due to the growth temperature and ion bombardment of the sputter deposition process.[25] The premixed layers reduce the quantity of available reactants and can thereby decrease the propagation velocity when bilayer thickness is on the order of the premixed layer thickness.[24] Most multilayer designs tested in this study have a large bilayer thickness compared with the premixed thickness.

From Fig. 3, it is apparent that the metal layer constituting the surface of a multilayer has an influence on laser ignition threshold. The ignition fluence for Al-capped multilayers is 1.4–3.6 times greater than the ignition fluence for Pt-capped multilayers. The capping layer is thought to significantly affect the degree of energy absorption and dissipation into the multilayer system. Bulk reflectivity is 88% for Al and 70% for Pt at a wavelength of 800 nm,[23] and therefore reflectivity alone may not completely account for differences in the amounts of energy absorbed and dissipated into the multilayer system.

Since femtosecond laser ignition of Al/Pt multilayers is accompanied by laser ablation, one approach to gauge differences in the amounts of energy absorbed and available for stimulating ignition is to determine the minimum energy nec-

essary to remove the top layer, or the ablation threshold. To directly compare the ablation thresholds for both Al and Pt films in this study, we sputter deposited monolithic 2000 Å Al and Pt metal films[16] on thermally oxidized Si (100) substrates and exposed the thin films to a series of single pulses with fluences ranging from 0.1 to 3 J/cm^2. We then measured the depth of ablated craters for each fluence using white-light interferometry, and using a logarithmic fit, determined the critical fluence necessary to induce material removal from each metal surface. By this method,[18] we report ablation threshold fluences as 860 ± 70 mJ/cm^2 for Al and 540 ± 50 mJ/cm^2 for Pt. Our measurements did not allow us to discern both fluence regimes mentioned earlier. However, both measurements extrapolated from our high fluence data are within reasonable agreement with published threshold values for metals in the high fluence regime.[17–19] Considering the energy required to ablate Al is $\sim$1.6 times higher than for Pt, the ablation threshold of the capping layer may better account for possible differences in the amounts of energy dissipated into the multilayer and the corresponding fluences necessary to ignite a self-propagating reaction.

It is noted that the ignition fluences converge for Al- and Pt-capped multilayers at lower bilayer thickness. We suspect this convergence is related to bilayer thickness approaching the size of the optical penetration depth and the presence of premixed AlPt interfacial layers.

In summary, we have presented results of the first study of pulsed laser ignition for reactive multilayers to the authors' knowledge. Femtosecond laser fluences for igniting a self-propagating reaction were measured for different Al/Pt multilayer designs, showing a relationship between bilayer thickness and ignition fluence. The observed relationship is similar to the one between bilayer thickness and reaction propagation velocities, demonstrating relevance of atomic diffusion length on laser ignition. In addition, the capping layer significantly influences the ignition threshold.

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