DIRECT LASER MATERIALS INTERACTION I LASER ABLATION OF SUPERCONDUCTOR MATERIALS
AND LASER WELDING

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RUNNING HEADING Direct Laser Materials Interaction

ABSTRACT

This paper considers two applications of direct laser materials interaction, laser ablation of
superconductor materials and Nd:YAG laser welding. The laser ablation experiments with 355 nm, 10 ns
pulses have demonstrated uniform thin superconductor films. The film uniformity was improved
significantly by rotating both the laser target and the film support and by vertically dithering the laser
focus. The film stoichiometry does vary with laser fluence but is within 10% of the target material at high
fluence. Annealing of the thallium containing films restores lost oxygen. For the welding application we
have investigated the conditions that influence the melt depth. High speed photography has shown the
plume to consist of a series of regenerates pulses that move in a direction normal to the surface. The time
for plume initiation and the laser power threshold for plume formation are dependent on the substrate
material. The plume temperatures, dependent on the welding atmosphere, temperatures and melt
depths, are higher for the reactive gases, Ar and N₂, than for the non-reactive gases, He, Ar and N₂.

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INTRODUCTION

Processes as diverse as welding and production of superconductor films may take advantage of the unique properties of laser radiation. This paper reports the results of research in each of these two areas: the production of thallium containing high temperature superconducting thin films by laser ablation and laser welding. The first application requires short laser pulses (10 ms) and the second much longer pulses (8 ms). Consequently, the conditions under which the irradiated material absorbs the laser radiation are quite different. For the ablation process the local pressure during and shortly after the laser pulse may greatly exceed ambient. This results in the near explosive removal of the material in the irradiated region. The welding laser, on the other hand, heats the material slowly enough that acoustical processes keep the pressure in the irradiated region close to ambient. The welding laser does form an evaporative plume but it results from slow evaporation, not an explosive expansion.

Laser welding is a well developed technology. The objective of the research at Los Alamos is to develop sufficient understanding of the laser interaction process to bring more versatility to the technique. Laser ablation of superconducting materials is only a recent development. Our goal again is to increase understanding of the process. We wish to find conditions where the stoichiometry is preserved and the deposited films are of high quality.

LASER ABLATION OF SUPERCONDUCTOR MATERIALS

Applications of the new metal oxides based perovskite high temperature superconductors (HTS) are dependent in many instances upon the ability to fabricate superconducting thin films. A number of approaches, including sputtering, evaporation, and an evaporated deposition employing both elemental and compound sources, have been used to produce high quality HTS thin films. One difficulty with elemental sources is that the relative evaporation rates for each source must be kept constant throughout the deposition by independently varying the temperature and sputter rate. On the other hand, compound sources suffer from the fact that the various metals and their oxides have significantly different vapor pressures, and hence the electron sputter yield. The final composition of the film will also depend upon the source and the backside pressure and deposition rate etc.
Laser deposition can reduce or eliminate a number of these difficulties. A single source may be used, thereby lowering the need for multiple deposition systems. In addition, the rapid energy deposition possible with laser sources results in temperatures so rapid that volatilization and evaporation occur without significant elemental fractionation. In addition, laser evaporation can be used under a variety of processing conditions. Deposition pressure may vary from 0 to several atmospheres, and the substrate temperatures are restricted only by the physical properties of the target and substrate materials used.

A number of groups have demonstrated deposition of metal oxides thin films using Nd:YAG, excimer, and dye lasers. The majority of this work has been done with YBaCuO systems, although more recently some work has been done on BiSrCaCuO oxide systems.

We have recently demonstrated the production of superconducting YBaCuO films using the second-harmonic 532 nm output from a Nd:YAG laser. Earlier work had used a frequency doubler to produce 532 nm because of the large absorption coefficient shallow penetration depth and relative immunity from both slow thermal processes and particulate formation in the film at this wavelength. More recently we have turned our attention to the deposition of tantalum containing thin films because of the more desirable chemical, physical, and electrical properties of these materials. We will describe recent results on deposition conditions, plasma diagnostics, and microstructural properties, resulting from deposition at 500 mJ into both 28 and YBaCuO tantalum and tantalum oxide targets.

We were deposited in a 25°C stainless steel baffled enclosure with an additional port on one side for optical access as shown in Fig. 1. Pressure during deposition were typically maintained at a few Torr by a combinatorial pump. Bulk samples were further mounted on a stainless steel ring mounted at 15 rpm in order to ensure even deposition. The substrate was polished, cleaned, and mounted at a 57° angle in an oxide film on the opposite face. The substrate can be heated externally, and mounting to another part of the temperature variation is possible. The temperature of the substrate was measured to within ±1 °C. The heating temperature can be varied to within ±1 °C.

We are currently using tantalum oxide as the target material.
Laser pulses of 15.25 μs at 155 nm were generated by frequency tripling the Q-switched output pulses from a Nd:YAG laser equipped with tilted beam optics. Mild focusing produced a fluence at the sample surface of 1.15 J cm⁻² and a confocal parameter much larger than the film depth in these experiments. The laser was operated at 10 Hz, and deposition times were from 15 to 60 minutes. The final turning piece was tilted vertically at 21.1 Hz in order to etch the target surface evenly.

As deposited films were insulating and required a post-deposition anneal at 850°C for 15 minutes in a H₂-enriched atmosphere to compensate for film loss from the film. Subsequent annealing at 750°C in an H₂ atmosphere for 24 hours gave shiny black films with room temperature resistances between 10⁵ to 500 MΩ.

**Results**

Most evaporations utilized a laser fluence in the range 4-9 J cm⁻², utilizing the cleaning prism used in the experiment to pattern part of the target surface as seen in Fig. 1. This proved to be far superior to etching a single track at fixed radial distance which resulted in severe spatial distortion of the etched pattern as well as thickness and compositional variations in the films. Consequently, a more reproducible deposition rate was obtained as evidenced by Eq. 4, which shows a plot of film thickness as a function of deposition time for subsequent runs. The film thickness for the rotated substrates as measured with a stylus profilometer was uniform to ±10% over the area coated 1.5 cm². This was a marked improvement over the unrotated substrates.

Using the deposition process, a single pulse was typically removed from the bulk target and only one single-deposited film on the substrate. This corresponded to a deposition rate between 1.5 Å/s. The difference between the etch rate and the deposition rate was presumably due to the ablation and incorporation of material overlap of the ablation plume with the substrate. The deposition rate was determined by optical microscopy, and the deposition rate of the film as determined by optical profilometry was uniform to ±10% over the area coated 1.5 cm². The film thickness was measured with a stylus profilometer.
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155 nm as shown in Fig. 4. For both wavelengths, the films were found to be deficient in calcium and enriched in Ti relative to the starting material near the threshold fluence for deposition. Although this result can not be explained in terms of simple volatility or reactivity arguments, it is consistent with recent observations on Ba-Cu films. In our experiments, the stoichiometry approached that of the starting material as the fluence was increased. At five times the threshold fluence, the film deposition was stoichiometric within ±10% to that of the target material. At higher fluences, the composition is then relatively independent of fluence over a broad range. An upper limit on usable fluence is imposed at ≈ 150 cm² by the deposition of relatively large particles. As shown by scanning electron microscopy (SEM),

The as-deposited Ba-Cu films were invariably deficient in oxygen and required a post deposition anneal as described above. In order to develop an in situ deposition process, we are investigating a number of diagnostics on the laser-generated plasma, including optical emission and mass spectrometry. Representative mass spectrometry results are shown in Fig. 5, which shows how the dynamic range available in our measurements and some interesting aspects of the evaporation process. In particular, no Ba ions are visible in this spectrum. We were also unable to detect any negative ions containing Ba attached to the plasma. On the other hand, we were able to detect large quantities of other species, relative to metal atoms and ions, which suggests an explanation for the lack of oxygen in the as-deposited films relative to the target.
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High volatility of tellurium and its oxides. Future efforts in this laboratory will center on implementation of an activated oxygen source in an attempt to lower the processing and annealing temperatures required.

LASER WELDING

The laser welding process is used as a source of energy that heats the substrate material above its melting point to produce a weld. However, the process is complex because of variations between the laser beam and the material that may either increase or decrease the absorptivity of the substrate. During the melting process, a fraction of the incident laser energy is absorbed by the substrate. The remainder is reflected or absorbed above the surface by the plume, which forms if the surface temperature is sufficiently high. The plume consists of evaporated metal, hot atmosphere gases, and reaction products. At low laser power heating of the bulk metals is by thermal conduction from the laser heated surface. Conduction mode. At higher laser power, a vapor depression may form in the molten pool, which may greatly enhance both the energy coupling and the melt depth. This process is called keyhole formation or keyhole mode. Other processes that influence the energy coupling include absorption of laser radiation by the plasma, plume convection in the weld pool, reflection from the workpiece, metal thermal reactions in the plume or melt pool, scattering from particles in the plume, and defocusing effects caused by the changing index of refraction in the plume.

Control over the process depends on understanding the laser-material interactions and the energy balance involved in these interactions. With this knowledge, process diagnostics and enhancement techniques can be developed.

Most Nd:YAG welding lasers are pulsed. Most CO_2 welding lasers are continuous wave. The time-averaged energy density, melting, evaporation, and conduction during the Nd:YAG pulse are generally shorter than the laser pulse length. However, some pulsed lasers may be more efficient. Continuous-wave lasers have the advantage of a continuous beam, although they may produce different physical and mechanical properties in the weld compared to a continuous-wave weld.

In recent years, the development of pulsed CO_2 lasers and welding techniques have been the driving force in improving laser welding techniques. The experiments suggest the use of pulsed Nd:YAG and Nd:YAG lasers for welding materials that are difficult to weld with continuous-wave lasers.
was determined by atomic emission spectrometry and the melt depth by metallography. The experimental conditions evaluated include laser pulse energy, gas pressure and gas flow rate. The melt depth was correlated with gas composition and oscillations in the plume height.

**Experimental**

The Nd:glass laser used in the welding experiments had a maximum pulse energy of 40 J. The pulse rate for all experiments was 6 Hz and the pulse length was 10 ms. Careful measurements of the spot size showed that it varied somewhat with the pulse energy. At low pulse energy (1 J), the laser was 8.75 mm diameter; at 40 J, it was 2.15 mm diameter. For some of the experiments we report the average laser power and others the power density at the target during the pulse. For the former, the pulse energy is divided by dividing the average power by ten.

The high-speed cathode-ray experiments were performed with a 3M Physics video camera that sampled all of 24 frames per second and 6 images per frame. Consequently, the time between individual images was 0.1 s.

A setup showed in detail of the experimental layout for the spectroscopic experiments. The light from the weld plume was imaged onto the entrance slit of a 3.5 meter spectograph. The spectrally dispersed light was detected by a line gated photomultiplier array. The array would be gated to monitor events occurring over an interval determined by the duration of light from the plume. The laser pulse repetition rate or pulse were selected using fiber-optic cables and photomultiplier tubes. The output of the tube was recorded on a digital oscilloscope.

**Spectral Analysis**

The characteristics of the plume produced by the laser will be influenced by several properties of the laser itself. These include the fraction of the incident laser beam absorbed, the efficiency of the plasma heating, and the amount and the most important of these properties are laser wavelength and laser energy. The energy absorbed by the metal depends on the extent of it which the metal is covered by the beam. As the laser energy is increased, the weld metal temperature increases, and the weld metal temperature increases. The weld metal temperature increases, and the weld metal temperature increases.
thermal conductivity of aluminum (3 W/m·K) exceeds that of stainless steel (17 W/m·K) by about a factor of 100 and the metals significantly lowers the thermal conductivity.

Figure 7 shows a high-speed photograph of the plume formation above individual spot welds made in 316 stainless steel, 304SS, and commercially pure aluminum 1100 Al. These two materials were chosen to be representative of materials that highly reflect Al and highly absorb SS, the 1.06 μm light from the Nd:YAG laser. Each horizontal panel shows a succession of individual photographs of the plume which expands vertically above a horizontal sample surface. Each panel corresponds to a weld made by the laser pulse. The time between successive photographs is 83 μs. The sample surface does not show in the photographs because the camera’s shutter was adjusted for proper exposure of the plume, which was much brighter. A fiducial mark shown as a white block to the left of each photograph sequence marks the start of the laser pulse. The powers listed at the left are the average laser powers measured at a pulse duration of 10 ns.

The temperatures of the weld plumes on 1100 Al and 304SS were measured using neutral iron line spectral observation below 1000 °C, the concentration of iron in 1100 Al is below 1%, so these lines are not visible. A constant emission intensity is a sufficient indication of temperature. Figure 8 shows the temperature as determined by atomic emission spectroscopy at various times during the laser pulse. The laser pulse energy is the same for both materials. The more strongly absorbing 304SS target gives a plume temperature that is several hundred degrees higher than the aluminum target.

The time for the initiation of the plume is shorter for 304SS than 1100 Al because of the greater absorption of the steel sample. Figure 7 shows the initiation time measured from the photograph sequence of each sample. The average power of the 304SS sample was 10 W, the 1100 Al sample 4 W. An Al sample had a longer time for plume formation and was more heating the power from 0 to 10 W over 40 μs in the 304SS sample. The Al sample plume initiation is most likely due to absorption of the power in the 1100 Al target. The laser beam intensity measurements were in error. The temperature of the plume was measured by the optical emission spectroscopy that determines the temperature from the plume through the power emitted. The initial intensity of the plume was all at the 1100 Al sample. The maximum temperature was about 1000 °C.
Both of these rates are only a small fraction of the sonic velocity. For example, the rise rate for 304SS is 6.4% of the room temperature sonic velocity in air. The ratio of the rates for 304SS and 1100Al (37) is about the same as the ratio of emissivities: 2 to 4: for these two materials.

At high powers, the welding plumes for both materials tend to rise, expire, and reinitiates during the pulse. The occurrence of these oscillations appears to have an energy threshold and the number of plume pulses increases quickly for both materials with increasing power. Up to 22 plume pulses were counted on the 304SS sample and 18 on the 1100Al sample. Experiments with 5052 and 6061 aluminum showed similar effects. The threshold pulse energies appear to be the same for the three aluminum alloys, but the number of plume pulses for 5052 Al was about 2.3 that of the other alloys. The threshold energy for these plume pulses corresponds to a significantly increased melt depth and the onset of keyhole formation. The occurrence of the plume oscillations has been attributed to successive opening and closing of the keyhole depression; that is, oscillation of the melt pool.

Keyhole formation results in increased absorption because of multiple reflections of the incident laser radiation in addition to the dramatic increase in melt depth. We also see that the rate of rise of successive plumes is greater than for the initial plumes. This is particularly true for Al 1100. For 370 W average power, the rate of rise of later plumes is three times that for the initial plume. We conclude that the keyhole formation increases the fraction of the laser radiation absorbed by aluminum by about a factor of three.

**Effect of the Welding Atmosphere on Melt Depth**

The atmosphere above the melt pool is known to affect the welding process. For example, gases such as N₂ and H₂ in the cover gas during welding can be incorporated into the weld and lead to embrittlement. In this study, the effect of different gases on the melt depth, the workpiece was placed in a sealed chamber which was purged by different gases. In Fig. 6, the melt depths obtained as a function of laser power for 2500 W are shown in Fig. 6a and b for continuous welds on 1100Al and 304SS, which were made at 1.5 W with below 10% overlap between adjacent welds. The divergence of the laser beam was kept constant as possible during these experiments by adjusting the collimator diameter. The melt depth of the plume energy was measured from the melt pool depression, with the adjustment the spot never changed during welding.
Two distinct regions are evident in Figs. 10 and 11: At power densities below about 1.3 MW cm\(^{-2}\), there was a small but gradual increase in the melt depth with increased power density. Above 1.3 MW cm\(^{-2}\), there was a 5-10\% increase in the melt depth with a small increase in power density. Comparison of the figures in the low power regime shows that the melt depths in 304SS were about three times the melt depths in 1100Al at the same power densities. Also, for 304SS, the slopes of the curves at low power density are about five times greater than those obtained for 1100Al. Both these effects may be indicative of the greater thermal conductivity and reflectivity of aluminum compared to stainless steel.

Inspection of the figures also shows that at a specific power density, the welds made in air, \(O_2\), and \(SF_6\) were deeper than those obtained in the other gases. The greatest effects were for the 304SS welds in which melt depths in \(O_2\) and \(SF_6\) were 5-4 and 2.9 times, respectively, the depth obtained using He at a density of 1 MW cm\(^{-2}\). In addition, the rates of change of melt depth with power density were greatest for the more reactive gases. These differences are attributed mainly to the different reactivities of the gases.

As stated above, temperatures in the welding plume can reach 3500 K, which is sufficient to generate free oxygen and fluorine atoms that can react with aluminum or iron to produce heat. The reaction \(2Al + 3O = Al_2O_3\) for example is very exothermic with \(\Delta H = -400\) kcal mole\(^{-1}\). The energy required to melt the volume of the largest melt produced in 1100Al: 2 mm D x 1.8 mm W, is 323 J. This energy is generated if only 21\% of the aluminum in the melt volume reacts to form the oxide. Similar results apply to the formation of iron oxides and fluorides. Measurements of the temperature of the plumes produced in the different gases are presented in Fig. 12. These data show that the temperature is greater for the reactive gases, suggesting that energy is being released via a reactive mechanism.

The increase in melt depth obtained with the reactive gases could also be due to greater coupling of the laser energy into the metal by formation of the oxides. Aluminum oxide, for example, exhibits much stronger absorption at 1.06 microns than pure aluminum metal. Other gas properties, such as thermal conductivity, may have a role in determining the melt depth, but their effect is probably small. The thermal conductivities of \(O_2\) and \(N_2\), for example, are almost identical, but significantly deeper melt depths were achieved, as shown in Fig. 10. It is also possible that some as-yet-undefined parameter of the welding process, for example, changes in the spot size due to thermal lensing in the different gases, may account for these differences.

The information reported here but these effects are expected to be small.
The curves in Figs. 10 and 11 show that at powers above 1.3 MW cm\(^{-2}\), a new mechanism becomes operative in each gas that produces a significant increase in the melt depth. This dramatic increase in the weld depth at the higher powers is probably due to a change in the welding mode from conduction to keyholing in which the laser beam is effectively channelled into a vapor cavity within the melt via multiple reflections. In the keyholing mode, as noted in the previous section, the fraction of laser energy coupled into the metal increases significantly over that obtained in the conduction mode. The transition from conduction to keyhole mode is demonstrated in Fig. 13 which shows cross sections of welds made on 1100Al in argon and air at different laser powers. At 300 W, which corresponds to a power density of about 1.34 MW cm\(^{-2}\), the weld profile corresponds to the conduction mode. At 350 W (1.36 MW cm\(^{-2}\)) the onset of keyholing is evident with a significant increase in the depth-to-width ratio of the weld. The main effect of the reactive gases over the transition region appears to be a slight reduction in the power density at which the transition from conduction to keyholing occurs. Unfortunately, it is not possible to increase the power density above 1.36 MW cm\(^{-2}\) to observe whether the large increase in melt depth with power continues at higher powers.

Conclusion

The properties of the welding plume correlate with the characteristics of a laser weld. A prompt initiation and rapid rise of the plume indicates effective coupling of the laser radiation to the workpiece. The plume oscillations are also indicative of operation in the keyhole mode. We now have sufficient data and understanding to begin the development of diagnostics based on plume properties that can be good indicators of weld characteristics. The studies with different atmospheric gases show the importance of gas-metal vapor reaction in determining the heat input to the weld. This gives another degree of freedom that one can use in controlling the weld properties. As this research continues, the development of a computer model of the welding process will become a high priority. The development of improved heat deposition diagnostics, and the establishment of a more quantitative correlation between plume characteristics and weld properties, is continuing.
ACKNOWLEDGMENTS

This work was performed under the auspices of the United States Department of Energy. The authors appreciate the support of the management of the Los Alamos National Laboratory during the course of this research.
REFERENCES

1. See for example: **Novel Superconductivity** Wolf S A and Kresin V. J. Plenum NY 1987

2. Wu X D and Venkatesan T in *Chemistry of Superconductors* Rao N N ed 1987


A schematic of the experimental apparatus. The target and substrate are rotated at 60 rpm while the laser beam is deflected at 10°. Typical pressures in the deposition chamber were 1.3 Torr.

A micrograph 5 μm of the laser-etched dark and unetched bright parts of the target pellet. The 2 μm observable at the etched part of the pellet and characteristics of the starting material. The unetched areas is brighter due to a finer-formed diagram final sintering of the pellet.

Shows deposition thickness of the thin film vs deposition time at constant fluence and repetition rate. This indicates that a constant amount of material is being deposited with each laser shot.

The composition determined by Rutherford backscattering spectrometry as a function of temperature is shown by open symbols and filled symbols.

An example of the ablated plane showing dynamic range and sensitivity of the measurement for the same material is also tabulated beneath each graph.

A schematic diagram for the laser welding experiments.

High-power photograph of the ablated plane during a single Nd:YAG laser pulse. Time increases to the right, and the time between images is 4.1 μs. The label on the left margin is the average laser power.

The highest powers are 848 mJ for 304L and 417 mJ for 6061.

Temperature-time data from one recent versus time during a 14.5-J laser pulse for two different materials.

Time for initiation of laser plume versus average laser power for 4043 and several aluminum alloys.

Melt depth in 304L versus laser power density for two different atmospheres, 500 Torr from a source of overlapping laser pulses.

Melt depth in 6061 versus laser power density for two different atmospheres, 75 Torr from a source of overlapping laser pulses.

Melt depth for continuous welds in 6061 versus temperature of the laser plate. The laser power was the same for all points. The temperature variation was produced by turning the gas over the weld.

The left graph shows 5, 10, 15, and 20.

Weld profiles for two different gases for three different laser powers that span the three of 1.

In summary...
Film thickness vs. Deposition time

\[ T = 0.0037 + 0.1215t \quad R = 1.00 \]
RBS Normalized Cu Ratio vs Nd:YAG Fluence

![Graph]

- Ti 155
- Ca-155
- Ba-355
- Ti-52
- Ca-532
- Ba-532
- Bulk Stoichi
$\lambda = 447 \text{ nm} @ 5.7 \text{ J cm}^2$

- $^{134}$Ba ($2\%$)
- $^{135}$Ba ($6.6\%$)
- $^{136}$Ba ($7.9\%$)
- $^{137}$Ba ($11.2\%$)
- $^{138}$Ba ($71.7\%$)

$^{138}$BaO$^+$

$^{138}$BaO$^+$
Nd - YAG LASER PLUMES

1045S (7ms, 10pps)

150W
100W
200W
250W
300W
370W

1100AI (7ms, 10pps)

100W
225W
370W
PLUME TEMPERATURE DURING A LASER PULSE

304 SS—214W, 1100 Al—214W (Air Atmosphere)

**Temperature (1000 deg K)**

**Time (ms)**

304 SS

1100 Al
PLUME INITIATION TIME
Stainless Steel and Al Alloys

LEGEND
304 SS ■
1100 AL ▲
6061 AL ●
5052 AL ▲

TIME FROM START OF LASER PULSE (μS)

AVERAGE POWER (Watts)
LASER WELDS IN VARIOUS GASES
304 SS—OVERLAPPING WELDS

POWER DENSITY (MW/CM²)

MELT DEPTH (MM)

O₂
SF₆
Air
Ar
N₂
He

Figure 10
1100 AL-- MELT DEPTH VS PLASMA TEMP.

FE LINES, N2, AR, AIR, O2, SF6 (INC. TEMP)