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**Cluster Beam Deposition of High Temperature Materials**

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CLUSTER BEAM DEPOSITION OF HIGH TEMPERATURE MATERIAL

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ABSTRACT

In this proceeding we will present our latest attempts to utilize a Smalley-type metal cluster beam source, to generate novel thin films. This technique employs entraining, within a high pressure molecular beam expansion, the products generated from laser ablation of a rotating target rod. We will show how just such a cluster beam source can be used to generate a high temperature material within a molecular beam and deposit it intact on a relatively cool substrate. By tailoring the various expansion conditions (ie., expansion pressure, laser fluence, type of carrier gas, pulse delay, etc...) one can drastically effect the morphology and chemical nature of the surface generated. This technique has the promise that it may be able to fabricate a wide variety of thin films with obvious industrial applications (superconducting thin films, diamond-like carbon films, patterned or multi-layered thin films, etc...)

INTRODUCTION

Recently there has been much interest in the literature in the generation of metal clusters via laser ablation. Laser ablation has a distinct advantage, particularly in the case of refractory metal, since evaporation occurs within a short laser pulse during which a high temperature plasma is formed on the bulk target. A novel approach to these experiments would involve a technique which would not only provide a convenient source of the metal vapor but also allow the experimenter to select the chemical state of the metal. To achieve this goal, we cross the expanding plasma plume of ablated target bulk material with a beam of rapidly expanding gas. This gas pulse serves two functions: the first is that of simple transport in that the ablated material is seeded into the molecular beam and carried through a nozzle into the vacuum chamber where the substrate is situated. Secondly, and more importantly, the pulsed carrier gas is able to interact with the ablated material. This interaction can be merely physical, in that the inert carrier gas provide many collisions downstream of the ablation site, serving to cool the metallic clusters generated. This turbulent mixing also provides for a very homogeneous beam density which in turn creates a uniform thin film. Changes in expansion conditions (laser fluence, expansion pressure, nozzle geometry, etc.) can affect the cluster size distribution and in turn affect the morphology of the thin film generated.

However, by the appropriate choice of carrier gas this interaction can also be chemical, in that the carrier gas will react with the ablated material. It is therefore possible to chemically modify the state of the metal into a new form for subsequent deposition as a thin film. We can then take advantage of the laser generated plasma as a highly reactive medium to generate novel molecules within the beam and then deposit as thin films.

EXPERIMENTAL

All films were deposited with a Smalley-type source [1-3] which has had wide use in the field of chemical physics for the study of neutral metal clusters [4-6]. Our modified source consists of an aluminum source block mated to a commercial molecular beam valve (Newport BV-100) with a half millimeter nozzle, and is depicted in figure 1. The path of the expanding gas pulse passes perpendicularly (left to right in the figure) over the surface of the target rod.

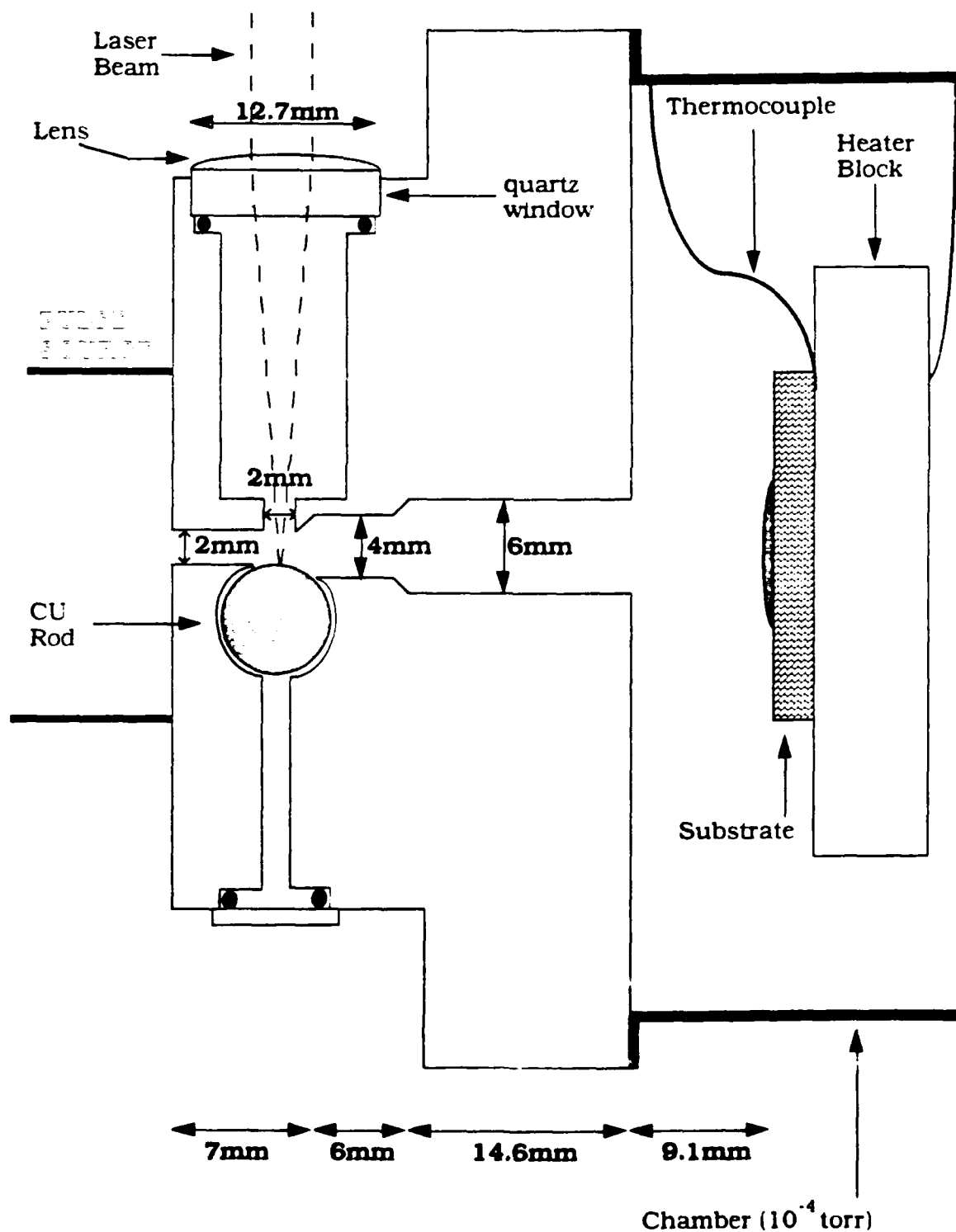


Fig. 1 Cluster beam source and film deposition chamber.

The ablation laser beam is the focused output of a 248 nm KrF excimer laser (Lambda-Physik EMG 150), and is mutually perpendicular to both the molecular beam and the target rod. The short (20 ns) laser pulse is tightly focussed onto the rod via a series of lens, with typical laser fluences ranging between 50 and 250 mJ/pulse, operated at 6 hz repetition rate. It is necessary for the target rod to be simultaneously rotated and translated such that each ablation event occurs at a new spot on the rod. For these initial calibration experiments a 1/4" copper rod was employed.

Coinciding with the laser vaporization, a gas pulse (1 ms in duration) is directed above the rod, such that the material ablated off of the surface of the target rod is entrained into the gas pulse and carried along through the expansion nozzle and into the vacuum chamber. This 'ablation region' is attached to the vacuum chamber via an expansion region 12 mm in diameter and 15 mm long with the substrate located in the path of the gas pulse 3 cm downstream. Typical backing pressures of the carrier gas were 40 psi with the deposition chamber pressure fluctuating between  $5 \times 10^{-4}$  to  $5 \times 10^{-5}$  torr.

Chemical composition, surface morphology, and film thickness of the deposited films were analyzed by ESCA, EDAX and SEM techniques. The films examined by ESCA, were deposited on glass substrates sputtered with a thin layer of gold and rolled stainless steel foil and were analyzed before and after deposition. The deposited films examined by SEM were sputtered with a thin layer of gold. These films were separated into two groups, the first of which were examined directly for surface morphology. The second group were used to determine film thickness in that the glass substrates were snapped in half and the film was examined by SEM on edge.

## RESULTS

The ESCA spectra of the deposited films indicated a qualitative difference between films deposited using different carrier gases. Films deposited using He, H<sub>2</sub>, Ar, or N<sub>2</sub> as carrier gas, and a copper rod as target, gave a characteristic pattern of metallic copper and visibly appear as a mirror-like film. In contrast, films grown in the presence of O<sub>2</sub> appear visibly rust-like and give a characteristic ESCA doublet pattern indicative of CuO.

The surface morphology, as characterized by SEM, was strongly dependent on the laser power used in the laser ablation. At higher laser powers (280 mJ/pulse) the surface is not smooth, being characterized by many circular 'platlet-like' structures as shown in Fig. 2A. At lower powers (210 mJ/pulse) these large features are essentially absent, and appears to be a relatively smooth copper film as shown in Fig. 2B.

From the films that were analyzed on-edge, a deposition rate of .4 microns per hour for copper ablated in the presence of He or H<sub>2</sub>. The rates for other gases (O<sub>2</sub>, N<sub>2</sub>, Ar) are estimated to be approximately 5 times slower.

## DISCUSSION

We observe that carrier gases such as He, H<sub>2</sub>, Ar, and N<sub>2</sub> when expanded over a copper target rod efficiently lay down a thin layer of metallic copper on a cool substrate. This is contrasted by the behavior for O<sub>2</sub> which generates a copper oxide film. This demonstrates that one may use such a source to chemically generate a new molecule, and lay it down as a thin film upon a suitable substrate. Since the high temperature chemistry (ie., oxide formation) occurs within the laser pulse within the source, the substrate is not subjected to the high temperature.

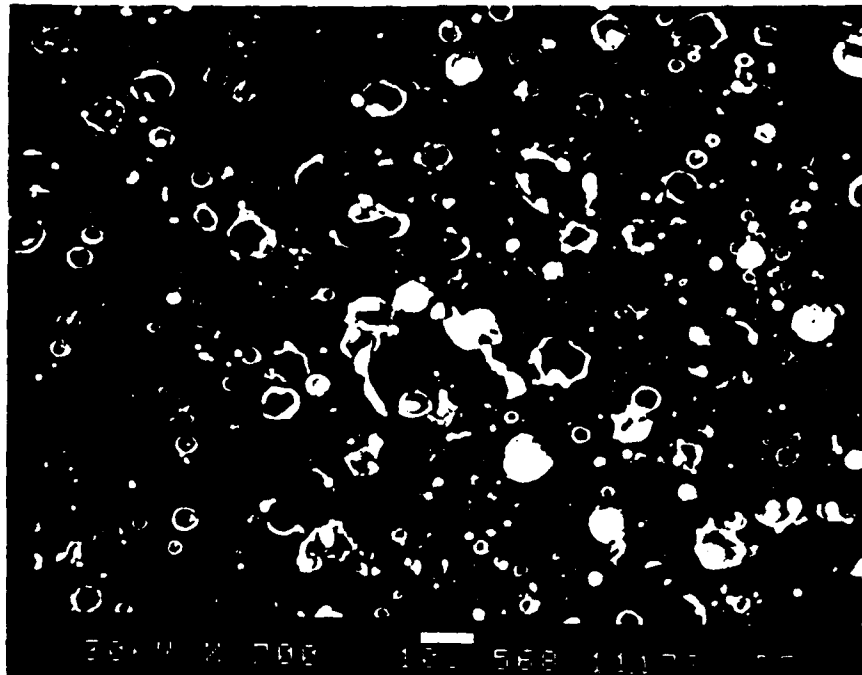


Fig. 2A Cu film run with H<sub>2</sub> as carrier gas, 280 mJ/pulse.

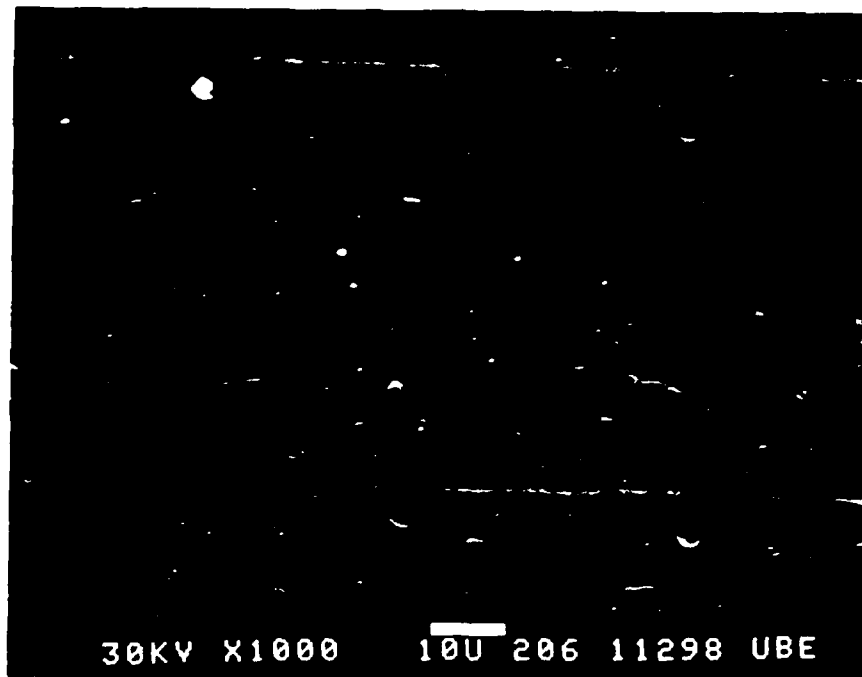


Fig. 2B Cu film run with H<sub>2</sub> as carrier gas, 210 mJ/pulse. Ripples in the film are due to ripples in the underlying stainless steel substrate.

The surface analysis was performed on the samples after the films had been removed from the vacuum chamber and stored under nitrogen for several days. One attempt to quantify the affect of atmospheric conditions of the metallic films involved the analysis of these films after varying amounts of storage times ranging from three days to three months. As a result, over time a copper oxide layer did slowly build up on the films deposited in helium, argon and nitrogen.

As well as chemical differences in the deposited films, physical differences in the morphology were seen as a function of laser power. At higher laser fluxes, the deposited films were dominated by circular 'platlet-like' structures of ablated material. We feel that this is due to large, 'microscopic' clusters of copper that upon impacting the surface spread out like droplets and freeze into this characteristic shape (Fig 2A). Reducing the laser power by 25% grossly reduces the copper cluster size and, as a result, these gross surface features disappear (Fig 2B).

The third qualitative difference is the higher deposition rates for metallic films grown under He or H<sub>2</sub> vs. other carrier gasses. One possible explanation is that with He or H<sub>2</sub>, a higher plasma temperature is achieved resulting in greater ablation of the bulk target rod. Further evidence for this has come from our new work in using this source to generate a high temperature superconducting thin film. Using a commercial YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> rod as our target, and He as the carrier gas, we observe (via EDAX) uniform thin films which have the stoichiometry 1-2-10 of Y-Ba-Cu. This indicates that at these high plasma temperatures the Cu is preferentially being ablated from the rod. Using O<sub>2</sub> or a He/O<sub>2</sub> mixture as the carrier gas we can now make films of the correct stoichiometry.

## CONCLUSIONS

We have observed several parameters which play important roles in depositing thin films with a Smalley-type source. The choice of the carrier gas gives control over the chemistry and composition of the film. In the presence of 'inert' gases, this technique was used to ablate a target material and deposit it on a cool substrate. In the presence of an oxidative carrier gas, the target material was not only ablated and deposited but it was also chemically modified. The physical surface morphology is also strongly dependent on expansion conditions. Changes in the laser fluence can lead to large changes in the appearance of the surface with a decrease in surface irregularities observed with a lowering of laser fluence. Lastly, the growth rate of the films was also strongly dependent on the expansion conditions with the fastest growth rate being observed for He and H<sub>2</sub>.

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