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1

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TITLE MECHANISMS FOR THE DEPOSITION OF THIN METALLIC FILMS BY LASER DRIVEN GAS PHASE

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# MECHANISMS FOR THE DEPOSITION OF THIN METALLIC FILMS
## BY LASER DRIVEN GAS PHASE REACTIONS

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ABSTRACT

   Gas phase processing makes laser deposition over large areas possible
but homogeneous nucleation of large atomic clusters must be avoided if films
are to be produced. Clusters can be highly variable in size from a few
atoms to significant fractions of a micrometer. If conditions do not allow
for complete quenching of the clusters produced in the gas phase, these
clusters can arrive at the substrate with sufficient energy to self sinter
into homogeneous films which are substantially different from metallic films
grown by thermal techniques. Using transmission electron microscopy (TEM),
we have characterized the microstructure of thin metallic films deposited by
laser breakdown chemical vapor deposition and identified a range of
deposition conditions which can lead from powders to homogeneous
polycrystalline films and mixed phase materials. Gas phase nucleation is
dependent on reactant partial pressures and the gas phase quench rate which
can be varied in part by adjusting the $H_2$ content of the source gas.
Manipulation of these parameters can vary powder size from about one
micrometer to less than 2 nanometers. Variation of the quench rate during
the deposition of polycrystalline films varies the grain size in the films.
Heating the substrate drastically changes the conditions under which the
film is formed and as a consequence, can radically alter the microstructure
of the film itself.

INTRODUCTION

   The use of gas phase laser chemical vapor deposition (CVD) techniques
holds substantial promise for large area, low temperature depositions in the
semiconductor and energy fields. However, films with suitable electrical
and structural properties must be produced. In these techniques, a laser
beam activates chemical precursors in the gas phase, resulting in chemical
reactions which lead to the deposition of a thin film. The substrate is
held at a temperature below that necessary for thermal deposition from the
precursors. Because the overall gas and substrate temperatures are low, the
possibility of homogeneous gas phase nucleation and growth exists. Indeed,
deposition results through a competing combination of gas phase and surface
processes. The control of gas phase nucleation is a key factor in the
applicability of these techniques to production processes.
   We have studied the effect of gas phase nucleation on the microstucture
of thin films deposited by laser breakdown chemical vapor deposition[1], but
the general conclusions of this study are applicable to other gas phase
laser techniques as well[2,3]. The microstructure of laser deposited films
is substantially different from that of thermally deposited films, which is
largely determined by surface reactions. The fine grain and equiaxed
structure exhibited by laser deposited films results from a combination of
gas phase and surface processes.
   The variables which control nucleation in the gas phase include the
partial pressure of reactant species, the overall pressure in the system,
and the quench rate or degree of cooling between pulses. In continuous wave
driven systems, the spatial thermal gradient between the excited volume and
the substrate plays a similar role to the temporal gradient in the pulsed

case. In the following sections, we will describe experiments which demonstrate the character of the deposition process and discuss the nature of the gas phase processes which occur.

EXPERIMENT

Mixed phase films consisting of fcc Ni and hexagonal $Ni_3C$ were deposited under a range of experimental conditions from $Ni(CO)_4$, Ar, and $H_2$. The microstructure of the films was determined by transmission electron microscopy (TEM) using a Phillips 400T instrument operating at 120 KV. Films were deposited on NaCl substrates at room temperature and floated onto Cu TEM grids. Films were also deposited directly on amorphous carbon films supported by Cu grids. There was no difference in the microstructures observed in the samples obtained from the two methods. Variations of gas composition, reactant partial pressures, total system pressure, and pulse energy were used to illuminate the mechanisms of film deposition.

A comparison of laser deposited films, with those deposited by conventional thermal CVD gives insight into the deposition mechanism. Figure 1. shows a thermal CVD film of tungsten grown at 450 C. While this film is much thicker than typical laser films, the dominant feature of strong columnar structure is apparent. This structure results from epitaxial growth on initial surface nucleation sites. By contrast, such columnar structure is completely absent from laser deposited films.
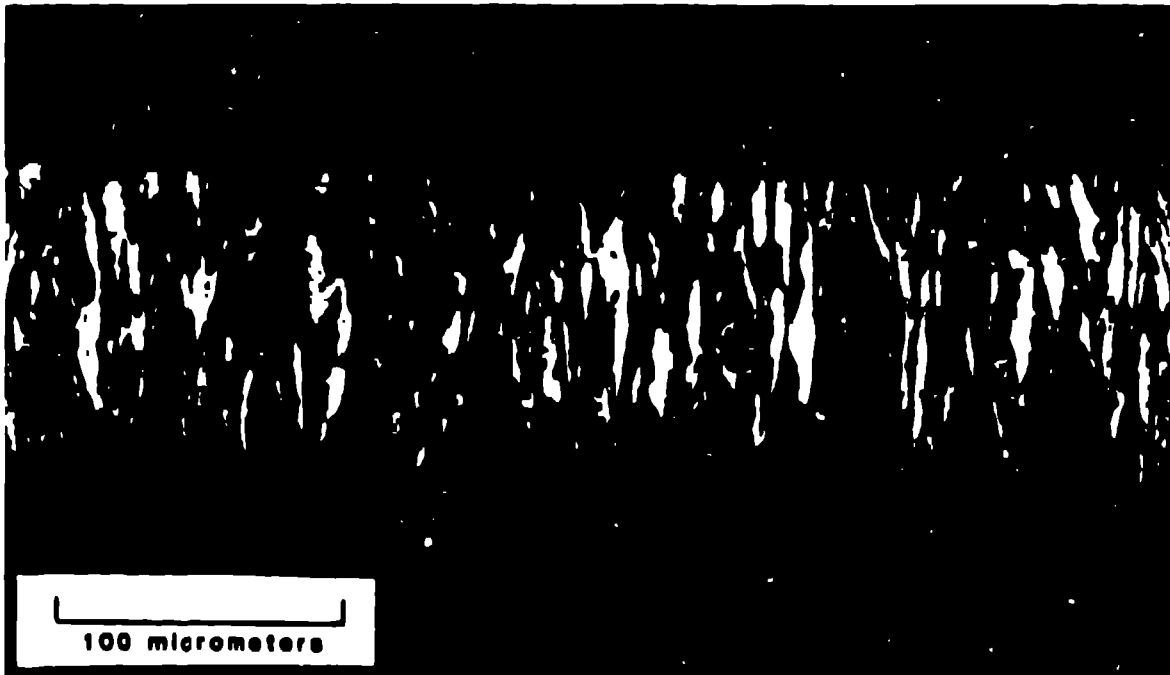


100 micrometers

Figure 1. Cross section of tungsten film grown by thermal chemical vapor deposition at 450 $^\circ C$ showing characteristic columnar epitaxial growth from heterogeneous nucleation sites.

Figure 2a is a TEM micrograph of a typical laser CVD film showing a uniform fine grained structure. In figure 2b, a darkfield image of the same film, the equiaxed nature of the grains is apparent. Darkfield images taken from several points on the same diffraction ring are similar, showing no evidence of directionally oriented growth. The epitaxy observed in

surface. In the case of laser deposited films, the low temperature of the substrate results in kinetic limitations to growth on the surface. Since growth cannot occur, or is at least severely limited, gas phase reactions which occur prior to the arrival of clusters on the surface become very important. The presence of metastable $Ni_3C$ demonstrates further the existence of these kinetic limitations[4].
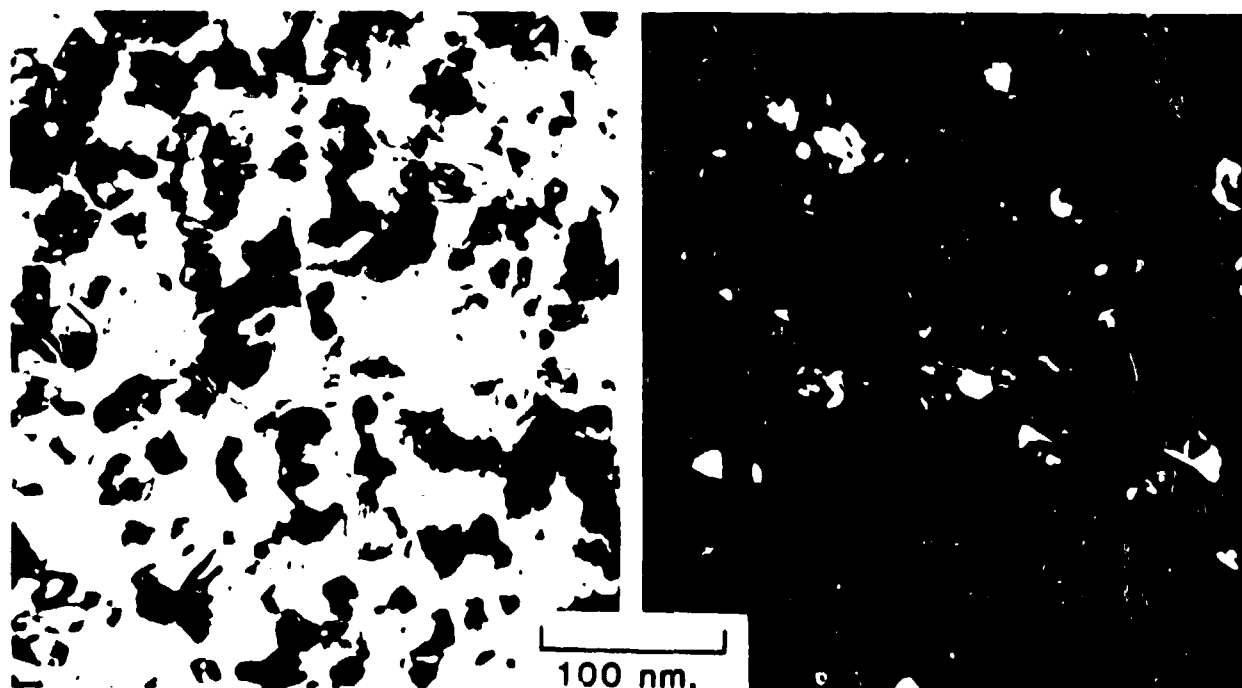


Figure 2. a) Brightfield transmission electron microscope (TEM) image of laser deposited film showing small size and uniformity of grains. b) Darkfield TEM image of laser deposited film. Images from different positions on the diffraction ring produce similar images, indicating equiaxed grains.

System conditions for laser breakdown CVD include a flow of carrier gas, typically Ar but this may include a reactive species such as $H_2$, a rather dilute metallic precursor, typically of the order of 1% in partial pressure, and a system pressure of the order of 10 Torr. Under these gas conditions, a breakdown plasma is generated in the duration of a 0.5-1.0 joule laser pulse (50-100 nsec). The temperature of this gas is quite high, greater than $10^4$ $^\circ K$, and it thermalizes rapidly, typically in a time less than 50 microseconds[5]. Losses from radiation and expansion then cool the plasma to a temperature of a few thousand degrees in at most a few tens of microseconds. The peak temperature of the plasma is important to the process only inasmuch as it determines the species available for subsequent reaction. For example, if the plasma temperature were sufficiently low in the decomposition of $Ni(CO)_4$, the volatile CO molecules would remain intact and no C incorporation would occur in the films. However, in laser breakdown plasmas, the temperature is so high that all molecular species are decomposed.

As the plasma cools, condensation of the reacting species occurs and clusters of atoms begin to form. This occurs at a temperature of about 2000 K for the system investigated here. The cooling rate from this point is critical to the process. If diffusion to the surface occurs quickly on the scale of the cooling time, the clusters will have sufficient energy to sinter on the surface, forming a homogeneous film. Alternatively, if the substrate is heated, sufficient atomic or molecular rearrangement can occur to grow a homogeneous film. The same effect can obtain if the deposition

are still occurring at the surface the heat released can cause further consolidation. If on the other hand the clusters lose energy rapidly on the time scale of diffusion, they will be "cold" by the time they reach the substrate and powder will be deposited.

For the conditions given above, the time necessary for a Ni cluster to diffuse to the substrate surface is of order $10^{-3}$ sec. In this time, the flow across the substrate travels about $10^{-2}$ times as far, explaining the observation that deposition occurs nearly symmetrically with respect to the beam, little influenced by the direction of gas flow. For all intents and purposes, the gas at a flow of flow of 200 std. $cm^3$/sec is stationary. In this same time, a Ni atom has had more than $10^3$ collisions with other Ni atoms, a value consistent with grain sizes of 10-100 nm. As the gas cools, the collision rate decreases, so the grain size is dependent on this cooling rate.

We have been able to manipulate the grain size in some films by addition of $H_2$ to the carrier gas stream. This results in a linear decrease in the grain size of polycrystalline films with increasing $H_2$ concentration. At temperatures below which Ni and/or $Ni_3C$ begin to condense, recombination of atomic hydrogen to the molecular form is already substantially complete. The heat of formation of $H_2$ released during this recombination thus does not effect the cooling process, and conduction is expected to dominate. Because $H_2$ has a substantially higher thermal conductivity than Ar, even relatively small concentrations of $H_2$ have a strong effect on the cooling rate. Other factors can also influence the grain size, including pulse energy and overall pressure which determine the peak plasma temperature and the mean free path respectively, and these factors make a detailed analysis of the process difficult.

The primary condition which leads to powder deposition is excessive reactant pressure. Often, particularly when powder particle size is large or if large agglomerates are formed, powder depositions are obvious as black soot. More subtle depositions of powder can occur in which the agglomerated particle size remains very small. In these cases, films appear metallic, but the deposits do not adhere to the substrate and high resolution microscopy reveals the particulate nature of the deposit. At concentrations of 50% $H_2$ or above, only powders could be produced. Very fine particulate deposits are formed when the cooling rate is manipulated to completely quench the gas in a time shorter than the diffusion time to the surface. Particle sizes as small as 1 nm with aggregates of 30-40 nm were obtained, indicating that the gas is substantially quenched within 150 microseconds[6].

The role of gas phase processes in laser driven CVD can be mitigated by substrate temperature. Clearly, if the substrate and/or gas temperature is high enough for thermal CVD, the laser beam is superfluous to the deposition process, though it can serve a useful role in nucleation if the beam is directed at the surface. However, at temperatures below that required for equilibrium growth, substrate heating can make energy available to overcome kinetic barriers to the formation of particular phases, resulting in coalescence of clusters on the surface, chemical reactions on the surface, or in phase transformations. Any of these processes can release energy to further drive the system towards equilibrium.

CONCLUSIONS

We have compared the microstructure of films grown by laser breakdown CVD with those grown by conventional thermal techniques and have concluded that gas phase reactions dominate the deposition process in the laser deposited films. Investigations of the effect of process variables on the grain size of laser deposited films indicates that cooling rates in the gas phase determine grain size and that if the gas is thoroughly quenched, film deposition cannot occur.

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