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Laser-induced coalescence of gold clusters in fluorocarbon composite thin films

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Abstract

The formation of conducting films from composite films comprised of gold clusters in plasma polymerized polyfluorocarbon (PPFC) is described. A focused, visible laser beam is used to coalesce the gold clusters within the PPFC matrix. Heating the composite with the laser causes the film to collapse with a loss of weight due to decomposition and volatilization of the polymer. Under the appropriate laser power and scanning conditions, coalescence of the gold particles results in a conducting metal line, exhibiting close to bulk metal resistivity.

1. Introduction

Laser patterning of thin films on solid substrates has been examined by a number of techniques, including pyrolytic decomposition of thin solid films [1,2]. This method consists of coating a substrate with a thin film which is generally composed of a polymer or a mixture of materials containing a metal. Irradiation of the film with a laser leads to heating and dissociation of the film, resulting in deposition of a solid material and evolution of gaseous by-products. The goal of this process is to generate a film of a pure material, such as a metal or dielectric. The process relies therefore on the thermal dissociation pathway of the initially applied film, and the various by-products which must volatilize and not decompose further to a solid substance.

We describe here a new technique which does not rely on a chemical reaction to form a metallic film but rather takes advantage of a physical transformation, the process of annealing or sintering of metal particles. The metal particles are initially embedded in a fluorocarbon polymer synthesized by a plasma polymerization process. The fabrication of metal/polymer composites by this technique appears to be quite general, and has been extended to a number of metal/polymer systems [3]. We have chosen a gold–fluorocarbon composite in order to maximize the "inertness" of the metal polymer interface towards chemical reaction. Heating of the film should in principle give rise to a purely physical transformation, the coalescence of the gold clusters, thereby giving rise to continuous metallic film under the proper heating conditions.

We report here the ability to generate conducting lines from these composite films, with a

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direct write technique using a scanning focused laser beam. The scanning takes place under ambient air conditions, with very fast scan rates, typically in the 0.1 mm/s range. The metal films obtained are a fraction of the thickness of the unreacted composite film. We have examined the coalescence process with several surface analytical and spectroscopic techniques in order to understand the mechanism by which the annealing takes place. In addition, the optical and physical properties of the thin dielectric films as the transformation matrix are described. The coalescence of gold clusters embedded in a fluorocarbon polymer has been examined with scanning electron microscopy, thermogravimetric analysis, energy dispersive X-ray analysis, and optical spectroscopic methods. The microstructure and DC conductivity of the films are analyzed as a function of gold volume fraction for as-deposited as well as laser annealed films. Periodicities in the generation of the continuous gold film are also described.

2. Experimental

Gold containing plasma-polymerized fluorocarbon films were deposited in a capacitively coupled, coplanar RF (13.56 MHz) diode reactor system [4,5]. The system consists of a vacuum chamber pumped by a turbomolecular pump to a base pressure below 10^{-6} Torr. During operation the turbopump is throttled with a variable aperture valve and the process gases are introduced via flow controllers to generate a pre-established pressure during the plasma-polymerization process. The RF power is applied via a matching network to the isolated electrode and the samples are fastened to the grounded electrode. In this configuration a sheath region with a substantial sheath voltage develops in front of the isolated (small) electrode. Due to the high sheath voltage this electrode (further on called target) is submitted to intense ion bombardment leading to the removal of atoms from the target by physical sputtering. In our case the target consisted either of a gold or a teflon (polytetrafluoroethylene: PTFE) target to deposit gold containing or pure polymer films, respectively.

A tetrafluoroethylene (C_2F_4)/argon gas mixture was injected into the discharge system with control of the total flow rate. Gold-containing films were deposited at a constant DC bias voltage of 1 kV at the gold target. For the deposition of pure polymer films a teflon target was used. The films were deposited on quartz substrates which are clamped to the temperature controlled, grounded electrode. The polymer deposition rate depends strongly on the sample temperature [6], and therefore it is of crucial importance for the reproducibility of the film deposition to carefully control the sample temperature. In these experiments the sample temperature was held constant at 15°C. The average deposition rate with this setup was 0.8 nm/s. The typical sample thickness was from 1000 to 20000 Å. The optical transmission of our films in the range from $p = 0$ (pure polymer) to about $p = 0.2$ was measured. The normal incidence optical transmittance spectra were recorded in a wavelength range from 200 nm to 3000 nm. The films were deposited on quartz samples and the film thickness was chosen to keep the maximal absorbance at 200 nm below 2.

Laser heating the thin films was accomplished with the TEM_{00} mode of a Spectra Physics Model 22–05 argon ion laser operating at 514 nm. The beam was expanded ($3\times$), collimated, and focused through a microscope objective (0.2 NA). The measured beam diameter is approximately 5 μm at the $1/e$ intensity points and was approximately Gaussian. The power available at the output of the focusing objective is approximately 5 W. Beam scanning was achieved by moving the substrate relative to the fixed final objective on a set of XY translation stages. The coalescence could be viewed in real time via a trinocular eyepiece located above a beam-splitting cube, on which a CCD camera with associated optics was mounted.

3. Thin film properties

The key property which controls the electrical characteristics both before and after laser annealing is the metal volume fraction of the deposited film. The gold volume fraction can easily be changed by adjusting the ratio of C_2F_4 to argon in the processing gas mixture and keeping all other process parameters constant. The gold volume fraction p of each film has been computed from its density $d(p)$ by using the relation $p = [d(p) - d(\text{polymer})]/[d(\text{Au}) - d(\text{polymer})]$ where $d(\text{Au})$ and $d(\text{polymer})$ are the bulk gold and polymer densities, respectively. The quantity $d(p)$ has been determined from the film mass by weighing the substrate before and after deposition and from the film volume calculated from the known area and the film thickness which was measured by the stylus method. For the gold density we used the literature value $d(\text{Au}) = 19.3$ g/cm^3 and for the polymer $d(\text{polymer}) = 2.0$ g/cm^3 was used [7]. The precision of p is estimated to be ± 0.03.

Many physical properties of the gold-containing composite films are pertinent to the generation of conducting films from the as-deposited dielectric film, and these properties are examined briefly here. The size distribution of gold clusters in the polymeric matrix is in the range of 20–80 Å. For regions which are somewhat smaller than the diameter of the substrate electrode, the dispersion of gold clusters within the polymer matrix is seen to be quite uniform by TEM studies (see Fig. 1). The films are very good insulators at a very low gold volume fraction, similar to pure PPFC. At high volume fraction of Au, the films are very good conductors, approaching the conductivity of bulk gold. The electrical percolation threshold lies at $p_c = 0.37 \pm 0.03$. In a narrow range of p around this percolation threshold the electrical properties of the films change from an insulator to a conductor which is accompanied by a drop of the electrical resistivity from about 10^5 $\Omega \cdot$cm at $p = 0.3$ to about 10^4 $\Omega \cdot$cm at $p = 0.5$ [4,5]. The optical properties of similar films over a wide range of gold volume fractions has been investigated and correlated with the microstructure of the films [8].

4. Laser annealing of gold micro clusters

We have fabricated composite thin films with a wide variety of gold volume fractions and have obtained data for each film over many conditions of laser heating. In many cases, conducting gold lines were formed, and we have found a number of experimental conditions which can lead to optimally conducting lines within the specific composite film. We have found by extensive SEM studies that the cluster coalescence and concomitant film collapse correlates with the conductivity of the annealed film. The extent of cluster coalescence can be controlled by scanning speed (dwell time) as well as the laser power. Composite thin films with conductivities below the percolation threshold have been fabricated, and in the majority of cases the laser was able to induce coalescence of the clusters to form a conducting line. This region of conductivity (below the percolation

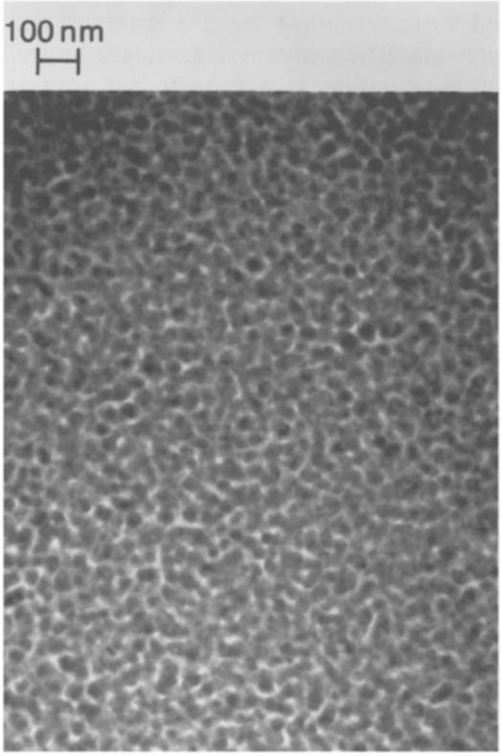

Fig. 1. Photographs of TEM images of Au/PPFC thin films at $p = 0.2$. At lower magnification the uniformity can be easily observed, and at high magnification (top right) the clusters can be seen to be approximately 50 Å in diameter. At this gold volume fraction, which is very close to the percolation threshold, and due to the thickness of the film it is difficult to observe the separation between individual metal clusters.

threshold) is the most interesting from an applications point of view because the film essentially behaves as a dielectric, and thus the region surrounding the conducting line behaves as an insulator. In the region of $p = 25$, where the as-deposited resistivity is approximately 10^{12} $\Omega \cdot$cm the laser-induced coalescence can form a conducting line with resistivity within 10% of the resistivity of bulk gold. The scanning velocity of the beam was not optimized for speed, and the highest scanning speeds achieved were up to 200 μm/s. The differences in the resistivities of the

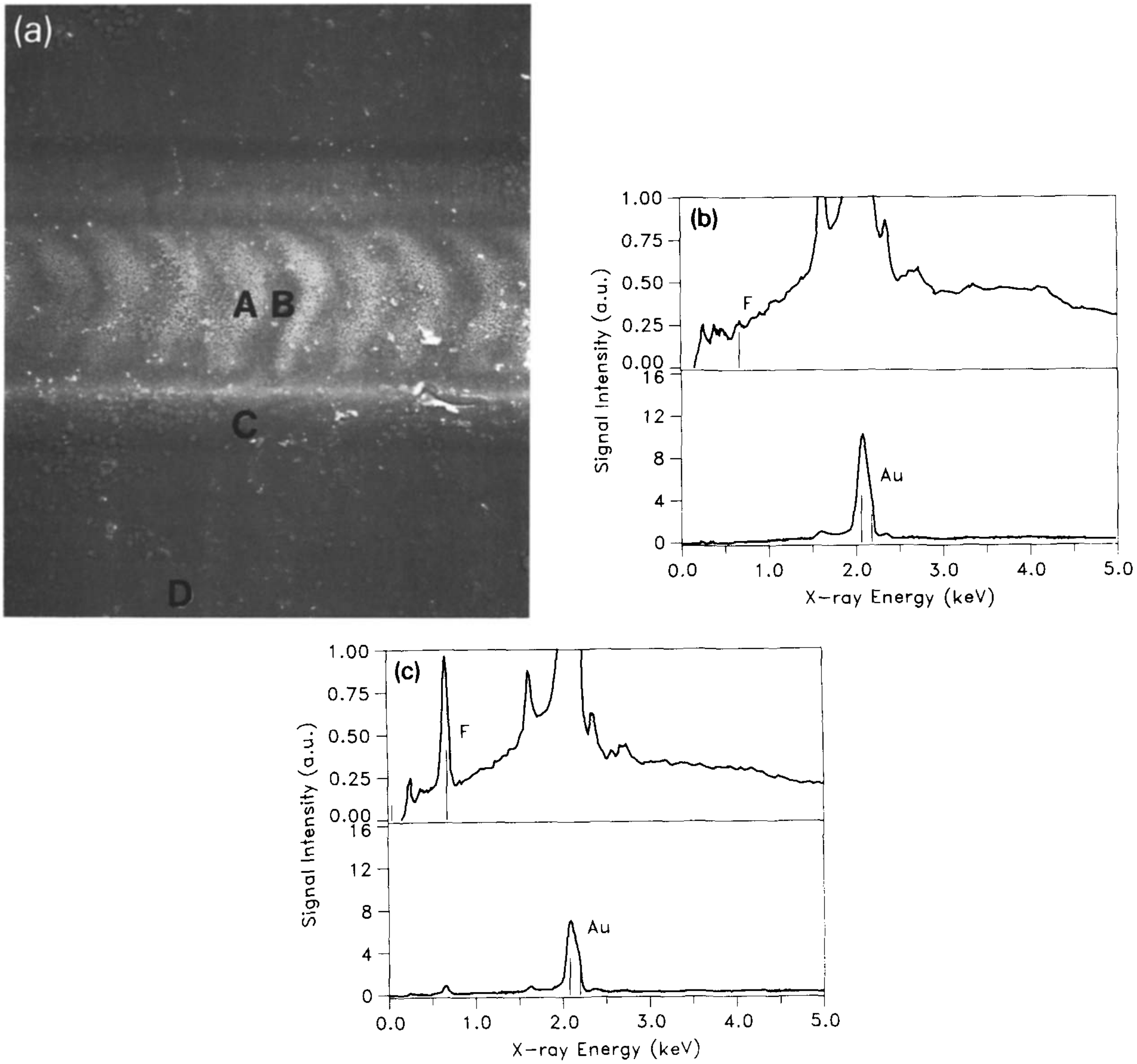

Fig. 2. (a) SEM photograph of the laser annealed Au/PPFC. The periodic features are due to the morphology of the film. In this film, the $p = 0.24$ with an as deposited film thickness of 16000 Å. The laser power was 76 mW at 514 nm. In the upper photograph, the linewidth is approximately 10 μm. (b) Energy dispersive X-ray analysis of the laser-annealed film in the B region shown in the SEM photograph above. The major line is gold, with trace amounts of other elements, including fluorine. (c) Energy dispersive X-ray analysis of the region C surrounding the laser annealed region. Fluorine due to the polymer is a major constituent in this region.

laser-annealed lines may be due to incomplete coalescence of the composite film and/or the morphology of the laser-annealed film [9].

At the higher p ($> 4\%$) clusters coalesce and the film collapses with a quasi-Gaussian profile, similar in shape to the laser intensity. The depth of the collapse is dependent on the dwell time and laser intensity, but at very low powers collapse is complete for most films. At $p = 4\%$, we have obtained data on the extent of film collapse at constant dwell time (or scan speed), but with varying incident power. The profiles show that the film collapse occurs in a continuous fashion, with the extent of collapse dependent on the incident power at constant dwell time. No build-up of polymer residue is noted at the side of the collapsed region except at the lowest laser powers used (< 20 mW). This behavior was observed for all p that we have studied except $p = 0$.

An aerial SEM image is shown in Fig. 2 of a laser annealed region in a composite thin film. The center region containing the letters A and B is the laser annealed region. An elemental analysis of the film by energy-dispersive X-ray analysis in the laser-annealed region B (as well as A) shows that within the analytical precision of this technique that the deposit is virtually fluorine-free, i.e. the conducting lines are metallic gold (see Fig. 2). Regions C and D adjacent to the laser annealed region and in the surrounding region, respectively, show large fluorine signals. The periodic features seen in the laser-annealed region in Fig. 2 are simply due to the surface morphology of the film, where there is a change in the reflectance of light. The periodicity of the features arises from an autothermal instability in the laser writing process, and is not due to a course x–y stage movement. This is a feature which we are presently examining.

Bulk annealing of the Au/PPFC films has been described in previous work [10]. It was shown that bulk heating led to film collapse from a metastable polymer state, with concomitant microstructural changes in the size and shape of the gold clusters. However, in the case of the bulk annealing experiments, all of the polymer is not removed (or volatilized). We have shown by thermogravimetric analysis studies that the amount of polymer removal is determined both by the temperature achieved during the heating as well as the initial gold volume fraction (see Fig. 3). This data shows that the higher p films have lost significantly more of the polymer fraction at a given temperature than the lower p films. This may indicate that the polymer chains in the composite are of lower molecular weight and are therefore more volatile, or it may also indicate that the higher p films are more reactive, with more unsaturated centers or dangling bonds due to polymer chains being terminated by the metal clusters.

With no gold microclusters ($p = 0$), the pure PPFC film has low optical absorbance in the visible region. High fluence is therefore necessary to achieve any transformation of the polymer at 514 nm. At high fluence, we observe by SEM a region of collapse with large amounts of solid debris surrounding the site. This finding indicates an ablative type of polymer removal when no metal clusters are present. Additionally, at very low p, the film does not coalesce in a straightforward manner as it does at higher loadings, but forms filaments or threads of gold which are oriented primarily perpendicular to the scan of

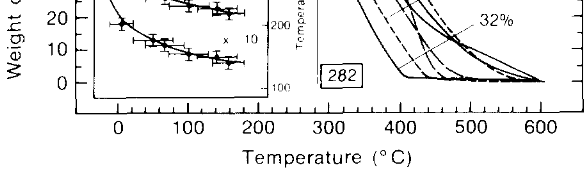

Fig. 3. Thermogravimetric analysis of the Au/PPFC film as a function of gold volume fraction. The percent figures are the gold volume fraction of the particular film. The inset graph shows the temperature at which a particular gold volume fraction film achieves a 50%, 25%, and 10% loss of the weight of the polymer fraction.

the laser beam. For $p > 0.04$, but for very high power and slow scan speeds, the coalescence becomes an unstable process, leading to gaps in the gold film that is formed. The residue of gold that remains near the gaps are generally spherically shaped nodules, indicative of complete melting of the gold film before a continuous film has a chance to form. These data indicate that optimal gold volume fractions for the laser writing process must be taken into account in addition to the as-deposited electrical conductivity, which optimizes the properties of the surrounding region.

An estimate of the maximum surface temperature induced by the laser is essential for an understanding of the physical and chemical mechanisms which are possible within the estimated temperature range. By assuming that the polymer undergoes simple volatilization, and the gold clusters migrate and coalesce to form a continuous film, we can estimate that with gold clusters of approximately 50 Å average diameter and $p = 4\%$, that after removal of 125 nm of film we have an effective $p = 100\%$ in the top surface layer, which is approximately 5 nm in depth. To a first approximation, this layer will absorb most of the visible light and give rise to a heated region which then volatilizes the film beneath it causing further collapse and additional gold coalescence. The beam diameter is much larger than this thickness of the gold layer, so we can neglect thermal losses through the gold layer, and use the thermophysical properties of the film/substrate. The beam is also larger in diameter than the thickness of the Au/PPFC film, and to a first approximation the thermal conductivity of the SiO_2 can be used as the surrounding heat sink.

The temperature rise can be calculated using the steady state expression [11]: $T_{max} = P(1 - R)/\pi r_f K_s$. In this expression P is the incident power, $R = 0.64$, the reflectivity of Au at 514 nm (12), r_f is the radius of the gold film at the coalescence zone, and $K_s = 0.02$ W/cm · K, the thermal conductivity of the quartz substrate. Using the range of laser fluence that generates good conducting lines, we estimate that the temperature rise extends from 70 to 280°C (i.e. between 40 and 200 mW of incident power). The actual temperature achieved could be somewhat higher for the following reasons. First, the reflectivity may be much lower because the films are not continuous and smooth as they are being formed. Second, the PPFC film has a lower thermal conductivity than the SiO_2 substrate, and this will lead to reduced heat loss. Finally, the annealing process is highly exothermic due to the formation of the metal–polymer composite in a metastable state by the plasma deposition process. The additional energy input due to the exotherm occurring in the matrix can be substantial and we have not taken this into account. We may regard the temperatures calculated as being lower estimates of the surface temperature maximums actually achieved during the laser annealing process. However, they give an indication of the approximate temperature range.

In order to gain an understanding of the physical and chemical phenomena involved in the laser-induced coalescence, we have examined the optical properties of the system by using a time-resolved reflectance experiment [13]. In this experiment we measure the specular reflectance at a fixed wavelength during a single coalescence event in the thin film. The change in optical properties is observed to occur under bulk annealing at approximately 200°C, very close to the glass transition (T_g) of PPFC. The optical change is correlated with the coalescence of the metal clusters, and can be described as taking place with the collapse of the polymer phase and migration of small clusters to form larger metal clusters. It has been determined previously that the size of the clusters (30–50 Å) can give rise to a strong change in transmittance in the visible region of the spectrum, and this is expected to induce a change in the reflectance of the sample as well, through a modification of the optical constants of the film. This effect is being further examined to quantify the physical transformations taking place during laser annealing.

5. Summary and conclusions

In this work, it is shown that bulk heating or annealing of the film leads to film collapse from a metastable polymer state, with concomitant microstructural changes in the size and shape of the gold clusters. Laser-induced coalescence of the gold clusters gives rise to metallic lines with approximately the linewidth of the 1/e intensity points of the laser beam. The extent of film collapse can be controlled be both scanning speed or dwell time as well as the laser power. At high gold loadings ($> 4\%$) the film collapses with a quasi-Gaussian profile, similar in shape to the laser beam intensity. The depth of the collapse is dependent on the dwell time and laser intensity, but at very low powers collapse is complete for most films. The polymeric matrix undergoes simple volatilization, and the gold clusters coalesce to form a continuous film. To a first approximation, the metal absorbs the visible light and gives rise to a heated region in the top surface which then volatilizes the film beneath it causing further collapse and additional gold coalescence. At the very lowest powers (< 30 mW) the resistance is far above that for a bulk gold sample, and as the power increases, the resistivity approaches that of bulk gold.

The technological significance of this work lies in the ability to directly generate microcircuit patterns in and on a Teflon-like carrier. The method is quite simple in that the films are formed in a one step dry process, and the metal line patterns are then directly written in a single subsequent step. The patterning step can take place in an ambient air environment. Gold conductors are equivalent in conductivity to copper, but are more robust to oxidation, and thus do not need passivation. In addition, the pure polymer films can be subtractively patterned with a single step laser exposure. The films can thus be built up into a three-dimensional structure with metal lines and/or vias, making this an extremely versatile system for microelectronic circuitry or packaging applications.

An analogous process, the laser sintering of powders has also been used recently to coat surfaces for fabricating three-dimensional objects [14]. In this process, an object or surface is coated with a powder, and a laser is directed at the region in space where material is to be added to the surface. The laser causes individual powder particles to consolidate or sinter, giving rise to a solid layer. Subsequent layers are then added and further processed. The selective laser sintering approach to solid fabrication has been applied to ceramics, metals, and polymers, with the largest emphasis to date on polymers. Because this technique is not very useful for metals, due to the extremely high temperatures needed to sinter metallic powders, we can now suggest the use of composite metal–polymer films as a solution to the high temperature problem. In the present case of Au–PPFC composite films, the temperatures needed to generate a metallic film are very close to the T_g of the polymer, a substantial improvement in processing conditions.

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