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Laser writing of high-purity gold lines

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Gold tracks of better than 98% purity have been deposited onto oxidized silicon wafers from gaseous methyl(triethylphosphine) gold(I), AuMe(Et₃P), by using 514 nm radiation from a focused cw argon ion laser. Room-temperature resistivities of 4.2 $\mu\Omega$ cm, comparable with bulk gold, were attained at a writing speed of 35 μ m s⁻¹. The track profiles suggest that deposition is more rapid on the gold surface than on the SiO₂ substrate.

Recent interest in the laser deposition of gold tracks¹⁻¹⁰ and patterns^{11,12} arises from their use in hybrid circuits, GaAs technology, and chip-to-chip integrated circuit interconnections. Each application has specific processing restrictions, so no single solution is likely to satisfy all problems. For example, gold-based ohmic contacts on GaAs or InP¹² require low deposition temperatures to avoid substrate decomposition, whereas screen-printed gold ink patterns on hybrid circuits require high annealing temperatures to produce the best electrical conductivity. Laser-induced decomposition⁴⁻¹⁰ of spin-coated gold-bearing inks and polymer films offers a possible solution to the spatial resolution limits $(\sim 100 \,\mu m)$ of conventional techniques for hybrid circuits. However, despite some successful experiments, the electrical conductivity is too low unless patterns are annealed¹⁰ above 250 °C. Adequate spatial resolution has also been demonstrated utilizing volatile gold(III) compounds such as dimethyl(acetylacetonate) gold(III)^{1/3,11} or trimethyl(trimethylphosphine) gold(III).¹² Resistivities of the gold deposits of 10-40 $\mu\Omega$ cm have been achieved³ but the highest conductivities were attained only at relatively low writing speeds.

In contrast to these previous studies, we have investigated the laser chemical vapor deposition of gold using *low oxidation state* gold complexes of the type methyl(trialkylphosphine) gold(I). In this letter we report specifically the deposition of gold tracks from methyl(triethylphosphine) gold(I) using 514 nm radiation from an argon ion laser.

The output from the Ar⁺ laser (Coherent Innova 100, 10 W) was focused to a 12 μ m (1/e²) Gaussian spot by a simple meniscus quartz lens. Feedback of a photodiode signal to the laser current supply maintained the laser output to + 0.5%. Laser irradiance at the substrate was measured to correct the monitor power meter for reflection losses in the optical train. Substrates were held orthogonal to the laser beam in an evacuable stainless-steel cell fitted with an optical quartz window. No internal heater was used, but substrates were either held by their edges or heat sunk onto a copper plate. The cell was mounted on a computer-controlled highprecision ($\pm 0.1 \,\mu\text{m}$) XY translation stage. The gold complex was a white crystalline solid, prepared by the reaction of chlorotriethyl phosphine gold with methyl-lithium in diethylether at -78 °C according to published procedure.¹³ It was stored at 22 \pm 2 °C under dry argon in a side arm of the

cell. Prior to deposition, the cell and side arm were evacuated to a pressure below 10^{-4} mB and subsequently the vapor pressure of the complex, at room temperature, was established in the cell.

Substrates were thermally oxidized silicon (100 nm of thermal oxide, according to ellipsometry) on (100) *n*-type Si wafers to allow electrical measurements of the deposits independently of conduction in the substrate. Morphology of the tracks was observed by laser scanning optical microscopy and scanning electron microscopy. Energy-dispersive x-ray analysis determined the elemental composition for elements heavier than fluorine. Laser ionization mass analysis (Cambridge Mass Spectrometry Ltd.) was performed in positive and negative ion mode. Tracks were profiled by a Dektak 3030 stylus instrument. Electrical conductivities were calculated from the track cross-sectional areas and measurements of the current-voltage characteristics according to automated measurements with a micron prober and a Hewlett-Packard 4140B test unit.

With a substrate translation speed of 35 μ m s⁻¹, deposition of gold lines occurred at laser powers above ~1.5 MW cm⁻². Figure 1 is a scanning electron micrograph of a series of these fine grained deposits. Note the absence of any ripple structure, which is commonly seen¹⁴ in argon ion laser deposited materials on these same substrates due to an inter-



FIG. 1. Series of gold lines deposited from AuMe(Et₃P) in the gas phase. The substrate was 100 nm thermally grown SiO₂ on crystalline silicon. Lines were drawn with an argon ion laser at $\lambda = 514$ nm at a speed of 35 μ m s⁻¹. Laser power is 1.5 MW cm⁻².

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ference effect between the plane-polarized laser beam and induced surface waves.¹⁵ At higher laser powers, >2.5 MW cm⁻², track centers were ablated and the gold was effectively redeposited at the periphery of the track. Linewidths increased with laser power, as shown in Fig. 2, using optical and stylus measurements, within a range of 15– 60 μ m for a constant translation speed. Deposit thickness increased from ~30 nm for the thinnest track at power ~ 1– 2 MW cm⁻² to ~70 nm for tracks deposited at the highest laser powers. Unexpectedly, line profiles of all the tracks did not reproduce the Gaussian temperature distribution in the substrate which is a feature normally associated with materials deposited using an argon ion laser.

The current-voltage characteristics of all lines were linear. Calculated resistivities were around $4 \mu \Omega$ cm, with negligible dependence on laser power. Current densities of $\sim 2 \times 10^6$ A cm⁻² were conducted by the tracks, representing the limit of the measurement electronics.

Energy-dispersive x-ray analysis confirmed that the deposits were of high purity (>98% gold) with no significant elemental impurities of atomic number greater than fluorine.

The more sensitive laser ionization mass analysis demonstrated that both carbon and oxygen concentrations were below the detectability limits of ~ 10 ppm. Peaks other than that due to gold were either due to the silicon substrate or were common surface contaminants (Na, K). A peak at mass/charge = 225 was attributed to the AuSi⁺ cluster ion. Due to the geometric effects of grain size and surface scattering¹⁶ in such thin samples, the electrical conductivity measurements cannot be expected to provide a reliable measure of purity. Elemental analysis, however, supports the initial supposition that carbon is not a significant impurity in our gold tracks.

In the present experiments we do not observe the common features of pyrolytic growth at low laser power densities. These include the interference ripple patterns mentioned previously, larger scale regular growth fronts at high powers, and a Gaussian cross section of the deposits. If the



FIG. 2. Variation of the width of the gold track with incident laser power. The scanning speed was constant at $35 \,\mu m s^{-1}$. Measurements were made with a profilometer and a scanning laser optical microscope. The inset shows a cross-sectional profile of a track obtained by profilometry.

substrate temperature under the laser beam is calculated according to the several models for laser heating by optical absorption,¹⁷ then it is essential to include all nonlinearities, such as temperature-dependent optical and thermal parameters. The virtually rectangular cross sections of our tracks suggest that a further feature should be considered, namely, the preferential growth from this precursor on a gold surface compared to silicon oxide.

A simple model for the deposition of gold tracks is proposed. The growth of nucleation sites follows the attainment of a critical substrate temperature. The latter requires an induction period which might be computed from the timedependent temperature profile induced by a translating cw laser beam. This would establish the threshold power for deposition and would explain the track width dependence on laser power but would not predict the subsequent growth rate. Since the growth of gold is supposed to occur via an organometallic species adsorbed on the substrate surface rather than via homogeneous gas phase decomposition, calculation of the volume growth rate requires further information on the heterogeneous decomposition of either the complex or intermediates. The importance of heterogeneous decomposition of organometallic compounds has been previously identified^{18,19} and present evidence of slow growth on clean glass surfaces, as well as the track profiles themselves, confirms this. No information is available on the postnucleation mechanism of thermal decomposition of complexes $Au(I)R'(PR_3)$, where R and R' are alkyls. On the basis of estimated bond dissociation energies, we suggest the following tentative sequence of reactions:

$$AuMe(PEt_3) \rightleftharpoons PEt_3 + AuMe$$

 $AuMe \rightarrow Au + Me$.

Because there is negligible carbon incorporation in the gold tracks, the methyl radical generated probably forms methane and ethane as the primary volatile products. Further work is required to identify the products of the reaction.

In summary, high-purity gold tracks with a resistivity of $\sim 4 \mu \Omega$ cm have been deposited by an Ar⁺ laser beam from an organogold compound at a writing speed of 35 μ m s⁻¹. No further thermal treatment was required and the deposition was localized in the vicinity of the focused laser beam, providing a line resolution of $\sim 15 \mu$ m from a beam diameter $(1/e^2)$ of 12 μ m.

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