# Laser-induced metal deposition on semiconductors from liquid electrolytes

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Maskless deposition of gold and copper from electrolyte solutions onto *n*-doped semiconductors (GaAs, Si) is investigated. The metal deposits are found to have lateral dimensions of about 1 $\mu$m and are in barrier contact with the semiconductor. The proposed deposition mechanism is governed by the electric fields resulting from the Dember effect, the *p-n* junction, and the thermal emf.

Laser-induced microchemistry is one of the most important alternative methods for the fabrication of different electronic devices.[1,2] Maskless laser-induced deposition of metals onto semiconductor surfaces is a field of growing interest because of the necessity to provide well-localized (1 $\mu$m) deposits with good conductivity, and with a controllable type of contact (ohmic or barrier). Deposition from both gaseous[3–7] and liquid[8–10] phases has advantages and disadvantages, depending on the application.

Until now, two mechanisms for laser-induced metal deposition have been described for electrolytes containing metal salts: (1) photochemical mechanism[11,12]; (2) thermal decomposition mechanism.[13,14]

In this letter we present experimental results concerning metal deposition onto semiconductors from liquid electrolytic solutions. The advantage of the present method is that it is a simple technique which produces quality, reproducible results. It is also amenable to theoretical treatment, which will be the subject of a subsequent paper.[15]

The experimental setup is shown schematically in Fig. 1. We used a copper vapor laser in a projection microscopic configuration, which also initiated the deposition.[16] This setup permitted the real-time observation of the deposition process on a screen, with linear magnification of about 1000-fold. The laser pulses ($\lambda = 510.6$ nm, $f = 10$ kHz, $\tau_{pulse} = 20$ ns) had an average power 1–5 mW and were focused on the semiconductor wafer surface. The spot size diameters were in the range 1–10 $\mu$m. The samples (*n*-Si and *n*-GaAs with $n = 10^{18}$ cm$^3$) were put into a dielectric cell filled with the metal salt solution [$CuSO_4$ or $KAu(CN)_2$ standard electrolyte]. No external electric field was used in our experiments. A computer-driven *x-y* stage allowed the appropriate scanning and positioning. The samples with deposits were submitted for mechanical, microscopical, and electrical investigations.

Single crystalline *n*-type GaAs wafers with parallel 100 surfaces and without any precoating were used. Among many possible electrolytes, $KAu(CN)_2$ was found to yield the best results for gold deposition.

The diameter of deposits at the initial stage of the process was found to be much smaller than the laser beam diameter. The main part of the deposit (nearly 80%) appears within 10–50 ms, and with a 1 s exposure time the deposit diameter reaches that of the laser beam. Thus the deposition rate decreases very dramatically with time.

The morphology of the deposit depends on the laser beam diameter. Deposits with lateral dimensions of about 1 $\mu$m appear as a succession of structureless hemispheres, as shown in Fig. 2(a). When the laser beam diameter is on the order of a few $\mu$m, a well-defined gap forms in the middle of the deposited region [Fig. 2(b)]. For even larger focal points, the middle part of the strip is filled with spherical metal particles.

Energy dispersive analysis by x rays reveals no contamination, indicating purity to within the 1% accuracy of the instrument (*K*, *L*, and *M* lines). The deposits prepared by this method represent rectifying contact with GaAs with a typical barrier height of 0.9 V. The conductivity of the ob-

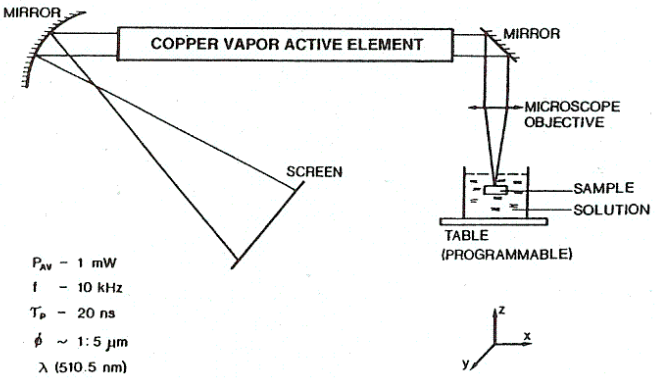


FIG. 1. Schema of the experimental apparatus.

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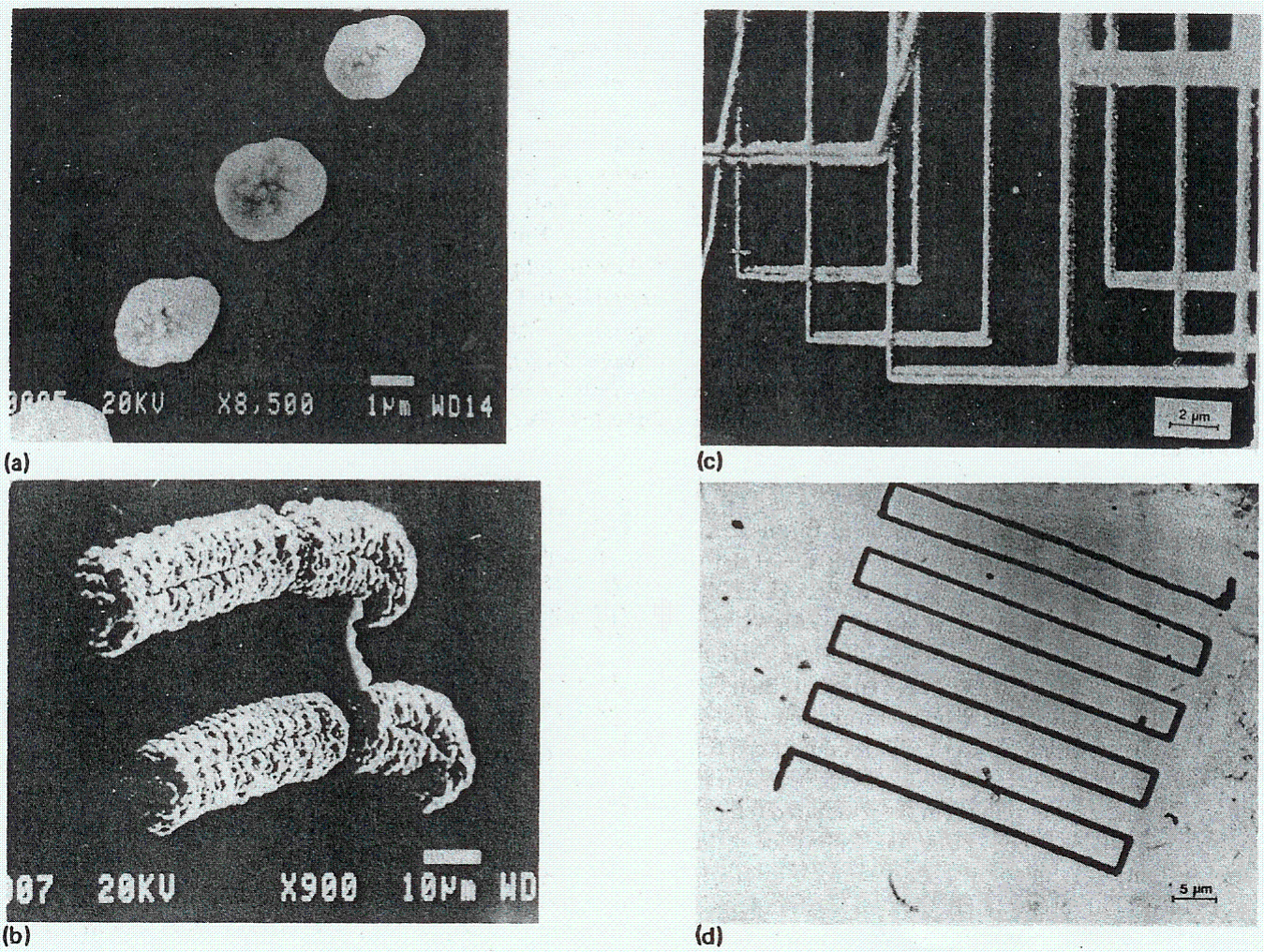



FIG. 2. Photos of deposits: (a) Au($n$GaAs) "hemispheres"; (b) Au($n$GaAs) with a gap in the middle of the deposited strip; (c) Cu($n$GaAs) deposit; (d) Cu($n$Si) deposit.

tained strips was found to be 2–3 times less than that of bulk gold.

Deposition of copper was carried out via the same technique as gold, using $CuSO_4$ in aqueous solution. Figures 2(c) and 2(d) show typical results of copper deposits on GaAs and Si, respectively. Copper deposition on silicon was successful provided HF was present in the electrolyte ($p$H = 1.5). In this case, a uniform copper film adsorbed loosely onto the Si surface even in the absence of laser radiation. Turning on the laser yields an accelerated deposition process with good adhesion (Scotch test).

The conductivity of copper deposits on both substrates depends on the scanning speed. At the slowest speed ($v = 20$ $\mu$m/s) it is half the value of the bulk material. At $v = 100$ $\mu$m/s it is one-sixth that of bulk copper. At high scanning speeds the effects of a single laser pulse can be observed. The resulting deposit has a typical height of 0.1 $\mu$m (Cu on GaAs at $P \simeq 5$ mW). Formally the deposition speed is $10^6$ $\mu$m/s, though it decreases after the first shot to 10 $\mu$m/s. Finally, the deposition width also depends on the scanning speed, as shown in Fig. 3. At an increasing scan rate, both the height and the volume of the deposit decrease slowly (Fig. 4).

We were unable to deposit either copper or gold on either $p$-GaAs or $p$-Si. Only intensive etching was observed in the illuminated area.

The photochemical deposition mechanism is known to be successful for metals with a negative electrode potential, such as zinc, cadmium, or nickel. This kind of deposition is probably only possible on $p$-type semiconductor wafers.[11,12] For electrodeless deposition, the laser illumination creates a cathodic region in the illuminated area and an anodic region elsewhere. For the $p$-type semiconductor, the cathodic depo-

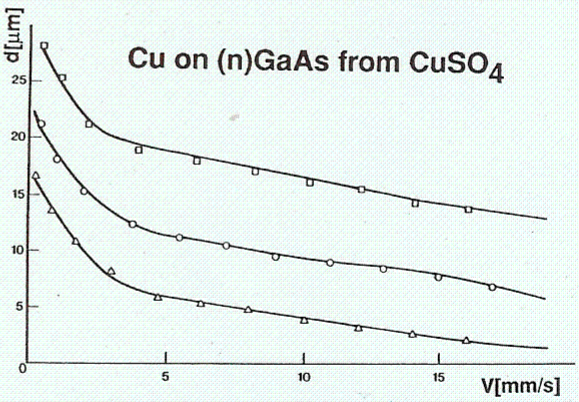
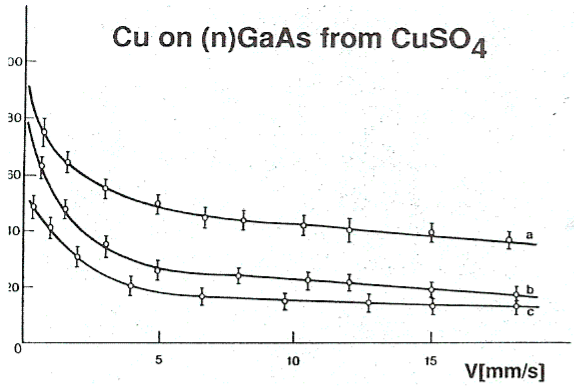



FIG. 3. Dependence of the deposit width on scanning speed for Cu($n$-GaAs): $P_a = 6$ mW, $P_b = 8$ mW, and $P_c = 10$ mW. Similar results obtain for copper deposited on silicon. The curves represent a least-squares fit to the data.




. 4. Dependence of the deposit volume on scanning speed for Cu($n$-.s): $P_a = 6$ mW, $P_b = 8$ mW, and $P_c = 10$ mW. The curves are a least-res fit to the data.

ɔn reaction occurs in the conduction band through the t-produced carriers. Conversely, the anodic metal strip- ɡ takes place in the valence band in the dark region.

Considering the experimental conditions for GaAs, it is r that each laser pulse produces nonequilibrium carriers ı energies $E \approx h\nu - E_g \approx 1.7$ eV. These transmit their en- / to the lattice, resulting in a temperature increase of ut 20 K, which corresponds to a thermal emf between the ted and nonheated areas of about 80 mV. We note that in case of $n$-GaAs the holes remain in the irradiated region; trons move outside. The potential difference (the nber photo emf $U_D$) due to their different mobilities ($\mu_e \approx 8$ for GaAs) is approximately the same order of mag- de as the thermal emf. The value of $U_D$ depends on the eration rate $g_s$ and is about 200–300 mV. Its rise time ($t_{rD} \frac{2}{B}/D_a = 2.10 \times 10^{-8}$ s, where $D_a$ is the diffusion coeffi- t 50 cm$^2$/s) is comparable to the laser pulse duration.

In $n$-type wafers the thermal emf and $U_D$ are combined a $p$-$n$ junction at the electrolyte-wafer interface. There-, in the centers which are enriched in holes, the anodic tion takes place (semiconductor etching). Outside we e an electron-rich ring-shaped region in which the ca- lic reaction takes place. A similar situation occurs for l deposition from $KAu(CN)_2$. After the formation of an initial ring-shaped deposit (with proven barrier contact), the generated carriers are separated by a $p$-$n$ junction field (1 V at a few $\mu$m distance) and the deposition process takes place in the center also. Ring-shaped deposits are observed with relatively weak solutions (0.04 M $CuSO_4$). This deposition process can be stopped by imposing an electric field of appropriate polarity, as has been verified experimentally.

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