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Percolation of gallium dominates the electrical resistance of focused ion beam deposited metals

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Metal deposition through focused ion beam (FIB) based systems is thought to result in material composed of the primary metal from the metallo-organic precursor in addition to carbon, oxygen, and gallium. We determined, through electrical resistance and chemical composition measurements on a wide range of FIB deposited platinum and tungsten lines, that the gallium ion (Ga^+) concentration in the metal lines plays the dominant role in controlling the electrical resistivity. Effective medium theory, based on McLachlan's formalisms, was used to describe the relationship between the Ga^+ concentration and the corresponding resistivity. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4874342]

Focused ion beam (FIB) based techniques are of wide use in the semiconductor industry and play a critical role in applications including, e.g., metal deposition induced repair of integrated circuits,[1] cross section imaging of micro-fabricated devices,[2] electron microscopy (EM) sample preparation,[3] etc. FIB induced metal deposition has also been extensively used in electrical connection and concomitant measurements of nanostructures such as nano-tubes/-wires,[4–6] quantum dots,[7] and related devices.[8] Typically, for metal deposition Ga^+ constituted ion beams serve to decompose the metallo-organic (MO) precursors—which serve as the source for the metal.

However, a major issue in FIB induced metal deposition is the sub-optimal electrical resistance of the deposited metals (e.g., in the case of platinum,[9–11] gold,[12] coppper,[13] cobalt,[14] and tungsten[15]), where electrical resistivity values have been reported to be orders of magnitude higher than that of the bulk metal. It has been widely perceived[9–11,15] that contamination from the carbon of the precursors decreases the resistivity. We will show, based on extensive experimental investigations, that the resistance seems to be controlled by the implanted Ga^+ with the metal from the MOs playing a negligible role.

The FIB metal deposition process involves heating (typically to ~50 °C) the relevant MO precursor in a gas reservoir adjacent to the EM chamber, subsequent to which MO vapor is controllably passed, through a gas nozzle, into the vacuum chamber. It is thought[16] that the vapor molecules adsorb onto the substrate and are then decomposed through interaction with the ion beam. The decomposition of the MO precursors should result in metal deposition, the thickness of which should be proportional to the MO-ion beam interaction time, while the residual volatile organics are concomitantly removed through vacuum pumping. A few prior reports[17,18] have investigated the relationship of different beam parameters on the growth rate and resistivity of deposited metal lines. It was found[17] that the resistivity can be varied by orders of magnitude by varying the deposition parameters and the presence of Ga^+ has a positive[18] impact in reducing the resistivity of electron beam deposited Pt metal lines. While it was indicated[4] that a metal- insulator transition as a function of nanowire diameter occurs in FIB deposited Pt-C nanowires (with diameters in the range of 70–150 nm), the relationship of the resistivity variation with Ga^+ concentration was not mentioned.

We focus, in this Letter, on the electrical resistance of tungsten (W) and platinum (Pt) metal lines deposited in commercial FIB/Scanning Electron Microscopy (SEM) systems using Trimethyl (methylcycopentadienyl) platinum: $C_9H_{16}Pt$, and tungsten hexacarbonyl: $W(CO)_6$, as the respective MO precursor gases. During the deposition, the ion beam accelerating voltage was fixed at 30 kV, e.g., to minimize the contribution of the secondary electrons.[19] Four commonly used deposition parameters were investigated, viz., (i) *beam current*—which defines the total Ga^+ charge/unit time (in the range of 80 pA–2.5 nA for Pt and 80 pA–9.3 nA for W), (ii) *percentage of overlap* between adjacent beam spots (in the range of 0% to −150%), with positive values implying superposition and negative values indicating the extent of spot separation, (iii) *defocus*—a measure of the ion beam spread (in the range of 0 μm–150 μm), with respect to the sample surface as a reference, and (iv) *temperature* of the gas injection system (GIS), which regulates the MO vapor pressure (in the range of 42 °C–54 °C for Pt and 41 °C–62 °C for W).

Subsequent to depositing the W and Pt metal lines, the chemical composition of all the constituent elements was quantitatively analyzed through carefully following all the standard practices of energy dispersive spectroscopy[19] (EDS). The EDS peak intensities of the W/Pt, Ga, C, and O peaks, ratioed to the background intensity, were used to determine the elemental concentrations in the deposited metal lines using ZAF (Z: atomic number, A; absorption factor, F: fluorescence factor) based matrix corrections. The

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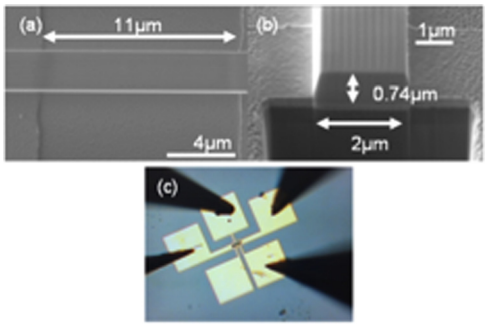

FIG. 1. SEM images of the (a) length (l), along with the (b) width (w) and height (h) of FIB deposited metal lines. (c) Optical image of the four-probe measurement of the electrical resistance on the FIB metal lines.

metal lines were contacted through Ti/Pd pads (patterned on plasma-enhanced chemical vapor deposited SiO_2 coated Si substrate) for electrical measurements: Fig. 1. The electrical resistivity (ρ) of the material was determined through four-probe measurements: Fig. 1(c), of the resistance (R) of the deposited metal lines (using a HP 34401A multimeter and a commercial probe station). The length (l)—Fig. 1(a), along with the width (w) and the height (h)—Fig. 1(b), of the metal lines were estimated from EM imaging and FIB cross sectioning.

We plot the estimated resistivity, ρ ($=Rwh/l$) with respect to M (i.e., W or Pt) and Ga at. % in Fig. 2. Generally, the ρ relates to the decomposition product of the MO precursor while EDS (used for determining the at. %) identifies elements independent of their chemical bonding state. Fig. 2(a) does not seem to indicate any clear correlation of ρ with at. % of M. For Pt (with bulk resistivity ~10.6 $\mu\Omega$ cm) metal lines, the ρ was noted to be in the range of 10^2–10^5 $\mu\Omega$ cm, with a metal concentration (as determined through EDS) in the range of 20%–40%. For W metal (with concentrations between 30% and 40%) lines, the ρ was found to be smaller[11] in the range of 100–400 $\mu\Omega$ cm, while still larger than that of the bulk W (~5.5 $\mu\Omega$ cm). However, a clear correlation of decreasing ρ, indicating increasingly metallic characteristics, with increasing Ga concentration was observed and is shown in Fig. 2(b). The Ga content was kept adequately low to avoid sputtering effects associated with larger fluences[20] at higher at. % Ga. The variation of the ρ with (M + Ga) at. % is indicated in Fig. 2(c), showing trends similar to Fig. 2(b). In Fig. 2(c), previously published[21] data have been superposed. While there seem to be some deviatory data in Fig. 2(c), their corresponding Ga concentrations—as in Fig. 2(b)—still conform to the trend of decreasing resistivity, indicating that Ga is the dominant factor in determining the electrical resistivity of the FIB deposited metal lines.

In order to better understand and model the electrical resistivity of the FIB deposited metal, the theoretical resistivity of the MO deposited metal-Ga-C composite was estimated through McLachlan's[22,23] general effective medium (GEM) based formulations,[24] developed as a generalization and expansion of Bruggeman's symmetric and asymmetric media theories for binary mixtures. We assumed that the mixture was constituted from two components—a low resistivity (ρ_{lo}) component (mainly from Ga with a resistivity of 27 $\mu\Omega$ cm (Ref. 25)) and a high resistivity (ρ_{hi}) component from C, un-decomposed MO precursor, etc. and that the variation observed in Fig. 2(b) corresponds to a percolative transition, where increasing Ga in the FIB deposited metal line decreased the overall electrical resistivity. While the symmetric theory was based on a random mixture of distinct spherical constituents, which completely fill the composite media (of resistivity: ρ_m), the asymmetric theory assumes concentrically coated constituents. The following form of the GEM equation was employed:

$$\frac{\varphi\left[(\rho_m)^{\frac{1}{t}}-(\rho_{lo})^{\frac{1}{t}}\right]}{(\rho_m)^{\frac{1}{t}}+\left[\frac{1-\varphi_c}{\varphi_c}\right](\rho_{lo})^{\frac{1}{t}}}+\frac{(1-\varphi)\left[(\rho_m)^{\frac{1}{t}}-(\rho_{hi})^{\frac{1}{t}}\right]}{(\rho_m)^{\frac{1}{t}}+\left[\frac{1-\varphi_c}{\varphi_c}\right](\rho_{hi})^{\frac{1}{t}}}=0. \quad (1)$$

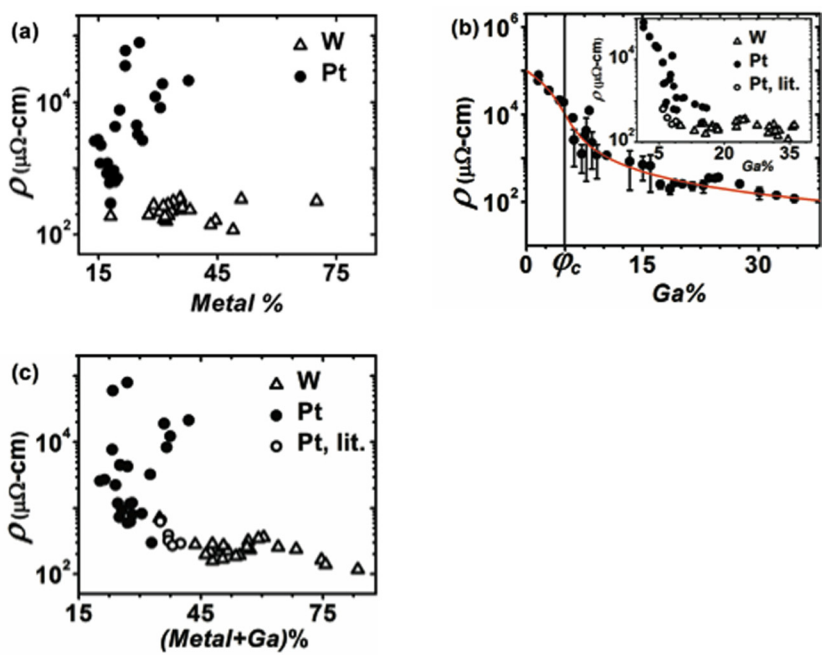

FIG. 2. The variation of the electrical resistivity (ρ) with (a) metal (M), (b) Gallium (Ga), and (c) conductor (M + Ga) concentration. The inset in (b) compares the experimental resistivity measurements from our work with previous literature. The red solid line in (b) represents the fit from the GEM based model to the experimental data (black solid circles). The percolation threshold volume fraction, φ_c is ~5 at. % Ga.

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In Eq. (1), φ is the atomic percentage of the low resistivity component (with φ_c being a critical atomic percentage of Ga at which a percolation path is formed through the medium) and t is a critical exponent. Equation (1) reduces to Bruggeman's symmetric and asymmetric media equations in the appropriate limits of the resistivity and shape of the components[23] and can also be viewed as an electrical resistivity percolation equation. For example, when $\rho_{lo} \rightarrow 0$, Eq. (1) reduces to

$$\rho_m = \rho_{hi}\left(1 - \frac{\varphi}{\varphi_c}\right)^t. \tag{2}$$

Alternately, with $\rho_{hi} \rightarrow \infty$, Eq. (1) yields

$$\rho_m = \rho_{lo}\left(1 - \frac{1-\varphi}{1-\varphi_c}\right)^{-t}. \tag{3}$$

Equation (1) could then be considered as a matched asymptotic expression[22] between Eqs. (2) and (3).

Extrapolating the data from Fig. 2(b) to 0 at. % Ga, the ρ_{hi} was chosen to be 10^5 $\mu\Omega$ cm. We could not preclude Ga ion beams and solely use electron beam deposition to determine this value due to fundamental differences in the underlying mechanisms, e.g., ions have orders of magnitude higher mass and a smaller penetration depth compared to electrons. The values of φ_c were estimated separately, using Eqs. (2) and (3) for low and high values of φ, and yielded $\varphi_{c,2}$ and $\varphi_{c,3}$, respectively. The difference $\Delta\varphi_c$ $(=|\varphi_{c,3} - \varphi_{c,2}|)$ was minimized through using an asymptotic $\varphi_c = 0.05$. Subsequently, Eq. (1) was solved numerically with MATLAB® for ρ_m and superposed on the experimental data of Fig. 2(b), with a $t = 1.3$. The sensitivity of ρ_m to a fitting parameter (say, α) was defined[26] through a ratio (S_α) of the unit change in the composite medium resistivity to unit change in the α, i.e.,

$$S_\alpha = \left(\frac{d\rho_m}{\rho_m}\right) \Big/ \left(\frac{d\alpha}{\alpha}\right). \tag{4}$$

For example, an $S_\alpha = 0.1$, implies that a unit change in α would yield a 0.1 unit change in the ρ_m. Equation (4) was evaluated, on the basis of Eq. (1), and plotted with respect to φ in Fig. 3. It was noted that φ_c could also be estimated from the extrema of the S_{φ_c} and S_t, given that φ_c determines the transition from the high to low resistivity behavior of the medium. Similarly, $S_{\rho_{hi}} \sim 1$ for $\varphi < \varphi_c$ implying a correspondence between ρ_m and ρ_{hi}, while for $\varphi > \varphi_c$ the correspondence is drastically reduced. A converse dependence was noted for the $S_{\rho_{lo}}$(indicating a match between ρ_m and ρ_{lo}), where the ratio tends to unity for $\varphi > \varphi_c$. The value of φ at the intersection of $S_{\rho_{hi}}$ and $S_{\rho_{lo}}$ could also be used to determine the φ_c.

In summary, we have shown that the concentration of Ga (the constituent in the ion beam) seems to be the dominant factor in determining the electrical resistance of FIB deposited lines. Extensive analysis (see supplementary material[27] for further discussion on the influence of ion-beam parameters on Ga content and electrical resistivity) has enabled us to conclude that it is the chemical composition of the deposited material that determines the electrical resistivity and not the FIB beam parameters *per se*. The beam parameters and other effects such as sputtering are all reflected through the chemical composition.

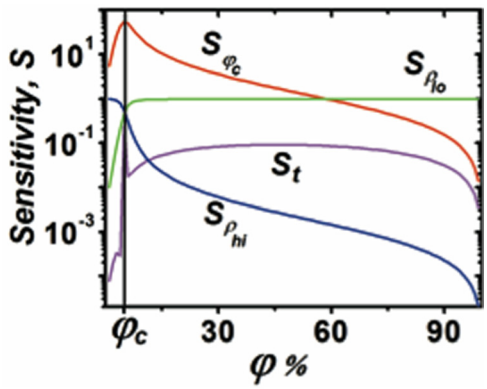

FIG. 3. The sensitivity (S_α) of the FIB deposited metal resistivity, ρ_m to the fitting parameters, α (= ρ_{lo},ρ_{hi}, φ_c, and t), as a function of the volume fraction, φ.

The surprising aspect was that the intended metal from the decomposition of the MO precursor does not seem to strongly contribute, presumably due to incomplete precursor decomposition. It may be suggested that, given the present limitations with precursor volatility and system stability, the deposition parameters that directly controls Ga^+ concentration may only be considered for tuning the resistivity of FIB metal depositions.

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[27]See supplementary material at http://dx.doi.org/10.1063/1.4874342 for further discussion on effective medium theory and the influence of ion-beam parameters on Ga content and electrical resistivity.

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