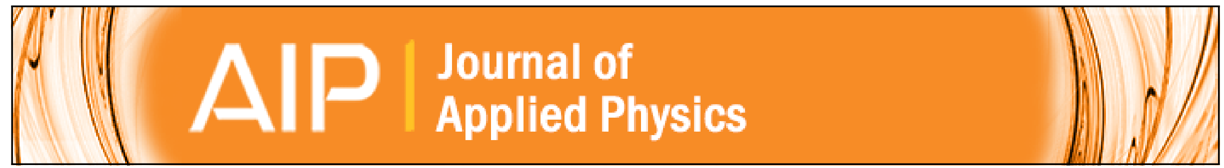

Reduced electrical impedance of SiO2, deposited through focused ion beam based systems, due to impurity percolation

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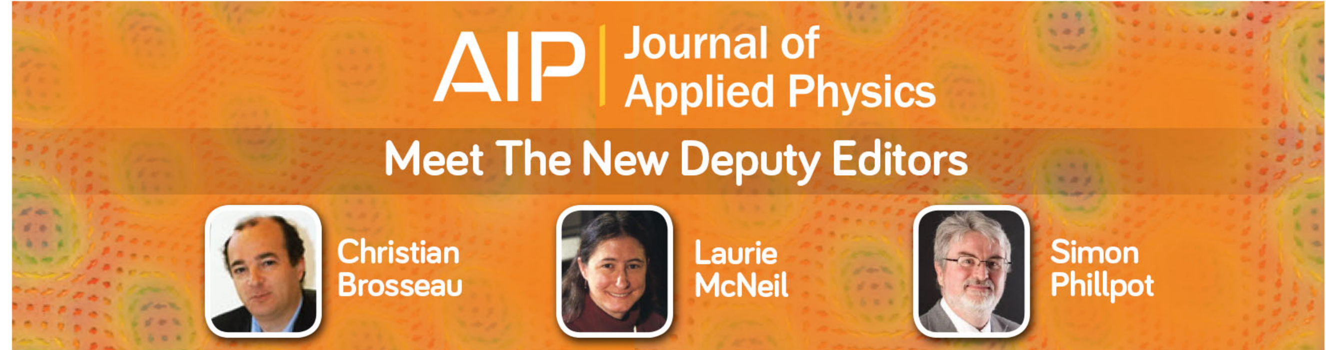

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Reduced electrical impedance of SiO_2, deposited through focused ion beam based systems, due to impurity percolation

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The electrical impedance (both the resistive and capacitive aspects) of focused ion beam (FIB) deposited SiO_2 has been correlated to the specific composition of the ion beam, in Ga- and Xe-based FIB systems. The presence of electrically percolating Ga in concert with carbon (inevitably found as the product of the hydrocarbon precursor decomposition) has been isolated as a major cause for the observed decrease in the resistivity of the deposited SiO_2. Concomitant with the decreased resistivity, an increased capacitance and effective dielectric constant was observed. Our study would be useful to understand the constraints to the deposition of high quality insulator films through FIB based methodologies. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4902521]

I. INTRODUCTION

Focused ion beam (FIB) based metal deposition is widely used in the semiconductor industry, e.g., in applications involving connection, restoration, and repair of integrated circuit based devices,[1–6] etc. Such usage implies site-specific deposition of metallic material from selectively dosed metallorganic (MO) precursor, which would need to be decomposed by the ion beam. However, it was previously indicated that *instead* of the metal constituting the precursor, Ga may be the deposited metal (e.g., when Ga^+ constitutes the ions in the focused *ion* beam). The basis of such a conclusion was that the percolation of the Ga seemed to determine the electrical resistivity (ρ) of the FIB decomposition product.[7] Such a result could arise from the typical parameters used for FIB deposition, in terms of the beam current (typically in the pA-nA range) as well as the temperature of the gas injection system (GIS). A restricted parameter range is used, as seems to be necessary for the adjacent scanning electron microscope (SEM) chamber stability. For instance, the FIB based metal deposition process involves heating, to only $\sim 50\,^\circ$C, the relevant MO precursor in a gas reservoir attached to the chamber, subsequent to which MO vapor is controllably passed through a gas nozzle into the SEM. It is thought[8] that the vapor molecules adsorb onto the substrate and are then decomposed through interaction with the ion beam. While the MO precursor decomposition should result in metal deposition, the thickness of which should be proportional to the MO-ion beam interaction time, this is not often observed and Ga concentration seems to be more critical in determining[7] the ρ.

Alternatively, FIB may also be employed for depositing insulating layers such as SiO_2 for interrupting or isolating the electrical interconnects.[9] For this purpose, ion beam induced decomposition of organosilicate precursors may be used. While a high ρ of the order of 10^{14} Ω-cm, corresponding[10] to the value for stoichiometric SiO_2, is desirable for such insulating films, the measured values of the FIB deposited oxide have been found to be much smaller by orders of magnitude. Considering the role of Ga in FIB based metal deposition, as previously discussed, it would be pertinent to investigate whether the presence of metallic Ga in the deposited SiO_2 may also be responsible for the reduced ρ.

While a few prior reports have explored the influence of FIB parameters such as current density,[1] role of oxygen,[11] variety of precursors,[12] etc., on insulator deposition, there has yet been no attempt to systematically investigate the underlying causes for the low resistivity[13] of FIB deposited oxide. It is the aim of this paper to address the primary influence behind the low ρ. The Ga and other impurity concentrations specific to the precursors are monitored with respect to their respective roles in determining the ρ. Additionally, the resultant electrical capacitance (C) variation, relevant to dielectric insulators such as SiO_2, is considered with an aim of understanding the influence of the impurities on the variation of the permittivity: ε_r.

II. EXPERIMENT

SiO_2 layers were first deposited using a commercial Ga^+ based FIB system (Vectra IET) deploying 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS): $(HSiCH_3O)_4$ as the organic precursor. The precursor was heated to $\sim 50\,^\circ$C and the vapor pressure (in the range of 0.5–1 Torr) controlled by the gas delivery system. Additional O_2 gas (in the range of 0–3.5 Torr) was concomitantly sourced in an attempt to improve film quality with the aim of oxidizing[8,11] any carbon containing co-deposits. Residual volatile organics were removed through continual vacuum pumping. During the deposition, the Ga^+ beam accelerating voltage was established at 50 kV to minimize the contribution of the secondary electrons.[14] The beam current (total Ga^+ charge/unit time) was

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fixed at 15 nA (maximum for the Vectra IET), and was chosen to obtain the maximum deposition rate. The overlap (separation between the centers of adjacent beam spots) was maintained at ~0.24 μm, which was determined to be optimal for uniform layer deposition. An alternative deposition methodology, where the SiO_2 was deposited using a Xe based plasma FIB system (FEI Vion PFIB) with 2,4,6,8,10,12-hexamethylcyclohexasiloxane (HMCHS): $C_6H_{24}O_6Si_6$, as the precursor was also used. The FIB accelerating voltage was kept constant at 30 kV (the maximum for the system), the pitch fixed to an optimal value of 0 μm and the beam current was chosen to be 15 nA, corresponding to that used in the Ga^+ based FIB deposition. The oxide deposition was typically carried out for a fixed time of ~40 min. A large variety of FIB parameters were used to obtain the used O/Si, Ga, C values (see Sec. I in supplementary material,[30] for more details on the parameters and obtained compositions).

The chemical composition of the constituent elements, independent of their chemical bonding state, in the deposited SiO_2 was quantitatively analyzed through energy dispersive spectroscopy[14] (EDS). The ratio of EDS peak intensities of the Si, Ga, C, and O peaks to the background intensity was used, with ZAF (Z: atomic number, A: absorption factor, F: fluorescence factor) based matrix corrections. The standard-less methodology used, yields absolute values for concentrations of all the detected elements (e.g., Si, Ga, C, and O)[14,15] precluding the need for normalization of the net concentration to 100%. Additionally, EDS measurement may better indicate the true film composition since the method is not surface sensitive. Consequently, the contributions of any surface contamination from ambient oxygen to carbon on the deposited material is negligible relative to the overall sampled volume.

For the characterization of the electrical impedance of the FIB deposited SiO_2, MIM (Metal-Insulator-Metal) based capacitor structures comprised of a Ti [50 nm]/Au [150 nm] top metal electrode, an intermediate deposited SiO_2 [200 nm to 1600 nm] insulator, and a Ti [50 nm]/Cu[250 nm] bottom metal electrode were fabricated on oxide coated Si wafers: Figure 1. As the variation of the ρ with the elemental composition, and not the electrical resistance, was considered the specific thickness of the oxide would not be important. A semiconductor parameter analyzer (Agilent B1500A) coupled to a commercial probe station, was used for recording the impedance characteristics (both the magnitude and phase) of the MIM structures over a frequency (f) range of 100 kHz to 1 MHz under an *rms* AC voltage of 100 mV. The electrical resistance (R) was deduced from the real part of the impedance, and the length (l) along with the width (w) and the height (h) of the metal lines (estimated from EM imaging and FIB cross sectioning) was used for obtaining the ρ ($=Rwh/l$) of the deposited material. The imaginary part of the impedance, i.e., $X_c = 1/j\omega C_{MIM}$, with $j=\sqrt{-1}$ and $\omega = 2\pi f$, was used for estimating the electrical capacitance (per unit area) of the MIM structures: C_{MIM} ($=C/wl$). The phase shift, θ ($=Tan^{-1}[X_c/R]$), was recorded as a measure of the relative resistive and capacitive contributions, e.g., $\theta \sim 0°$ is typical of pure resistance like behavior, while $\theta \sim -90°$ indicates capacitive characteristics.

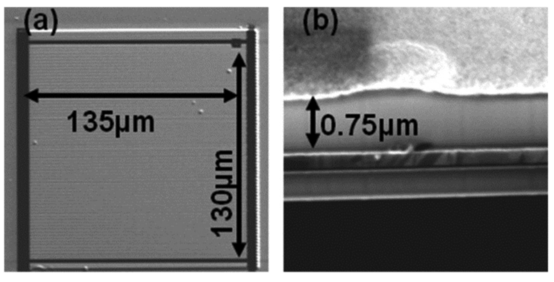

FIG. 1. SEM images of the (a) length (l), and the width (w), and (b) height (h) of the metal-insulator (Ga/Xe FIB deposited SiO_2)-metal devices used for the electrical impedance measurements.

III. RESULTS AND DISCUSSION

As an insulator for isolating metallic interconnect, it is desirable that FIB deposited SiO_2 have a very large ρ and electrical resistance. To monitor such characteristics, variation of the measured resistivity ρ as a function of the O/Si ratio is recorded: Figure 2. It is expected that stoichiometric crystalline SiO_2, with an energy band gap of ~9 eV, would correspond to a very large ρ of the order of ~10^{14} Ω-cm[10]. While a ρ maximum was indeed observed at an O/Si ratio close to 2, it was noted that the observed FIB deposited SiO_2 resistivity was orders of magnitude lower at ~10^7 Ω-cm. It was hypothesized that such a drastic lowering could have been caused by metallic impurities present in the SiO_2 layer. Given that an organic precursor (i.e., TMCTS: see Sec. II) was used, the only metal was Ga—the constituent of the ion beam. When the determined ρ was plotted as a function of the Ga content (determined from EDS): see Figure 3(a), a decreasing resistivity with increasing Ga content was clearly noted. Interestingly, such a decrease was also observed when the ρ was plotted as function of C as well: Figure 3(b). It was then thought that both Ga and C impurities could be responsible for decreased SiO_2 resistivity.

To determine whether Ga or C was more critical for the resistivity decrease of the SiO_2, a sensitivity analysis was performed. The sensitivity of ρ was defined with respect to the EDS determined atomic concentration, α through a ratio

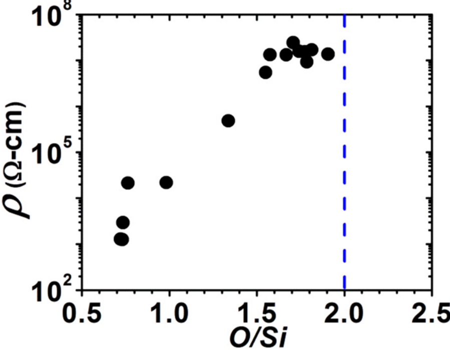

FIG. 2. The measured variation (data in black filled circles) of the electrical resistivity (ρ) of the FIB deposited SiO_2 as a function of the O/Si ratio (determined through energy dispersive spectroscopy). The dotted line indicates the stoichiometric O/Si ratio of two, where a ρ maximum would be expected.

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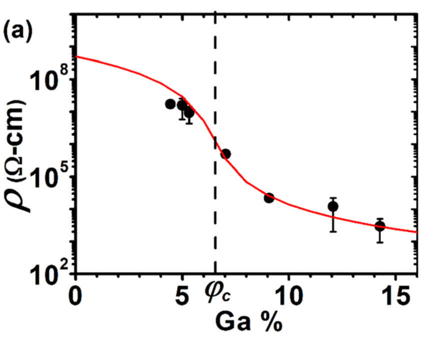


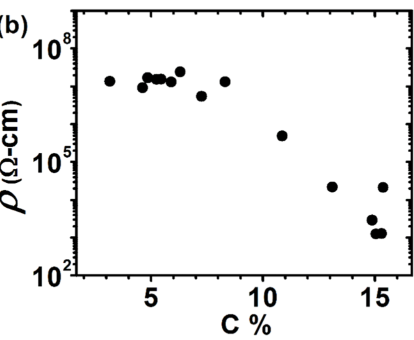


FIG. 3. The variation of the electrical resistivity (ρ) of the FIB deposited SiO_2 with increasing (a) Ga and (b) C content. The black filled circles indicate the experimental data, while the red solid line in (a) represents the fit from a GEM based model to the experimental data, with a percolation threshold, φ_c of ~6.5 atomic % Ga.

$S_\alpha = (\Delta\rho/\rho_f)/(\Delta\alpha/\alpha_f)$. Here, $\Delta\rho = |\rho_f - \rho_i|$, and $\Delta\alpha = |\alpha_f - \alpha_i|$, where ρ_f and ρ_f are the ρ values at α_f and α_i, respectively, with f and i denoting the compared quantities. From such an analysis (see Sec. II in supplementary material[30]), it was deduced that less Ga was required to achieve the maximum sensitivity. There also seemed to be a critical Ga content for the transition from a relatively insulating to a metallic state, as seen through a plot of the phase shift, θ with respect to the Ga atomic %: Figure 4(a). It was observed that, at low Ga concentration, the θ was $\sim -90°$ indicating dielectric/capacitive behavior and beyond a certain Ga concentration (~6%), θ was indicative of resistive characteristics, denoting the presence of metallic material.

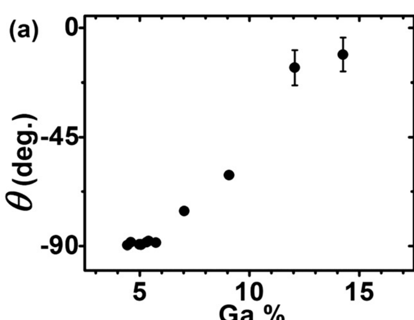
For further understanding of the decrease in the resistivity due to the increasing Ga content, concepts related to effective medium theory were considered. McLachlan's[16–18] general effective medium (GEM) based formulations,[19] developed on the basis of Bruggeman's symmetric (spherical constituents, e.g., Ga, Si, O, C constitute the composite/effective media) and asymmetric (assuming concentrically coated constituents: e.g., SiO_2 coated with Ga or C) media theories for binary composites, were adapted. It was previously shown that assuming a two component effective medium,[7] e.g., a low resistivity (ρ_{lo}) component constituted from Ga and a high resistivity (ρ_{hi}) component constituted from SiO_2, would result in a variation as observed in Figure 3(a) and corresponds to a insulator to metal based percolation transition for the medium, due to the increasing Ga. The following form of the GEM equation was employed:

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

In Eq. (1), φ is the atomic percentage of the low resistivity component (with φ_c being a critical atomic percentage of the component at which an insulator to metal transition by percolation occurs) and t is a characteristic critical exponent. Using the GEM model, a $\varphi_c = 6.5\%$ Ga was assumed as it was seen that the transition occurs between 6% and 7% Ga concentration Figures 3(a) and 4(a). The t was equated to a value of 2 corresponding to the standard percolation exponent[20] expected for a three-dimensional composite. The other two parameters ρ_{hi} and ρ_{lo} were taken to be 5×10^8 Ω-cm and 20 Ω-cm, respectively, in accordance with data from previous reports[21] and match the experimental data. Using the above parameters, Eq. (1) was solved numerically with MATLAB® for ρ_m and shown as a red curve in Figure 3(a), in correspondence with the experimental data. The excellent agreement of the GEM model based calculation with the data indicates that the FIB deposit may indeed be described as a two component effective medium.

While the role of Ga seems to be more important in reducing the SiO_2 resistivity, Figure 3(b) indicates a role for the C as well. To elucidate such influences, a Ga free FIB system was used to deposit the SiO_2. For this purpose, a Xe based plasma FIB system was used (FEI Vion PFIB) using $C_6H_{24}O_6Si_6$, as the precursor gas was used. As Xe ions are gaseous at room temperature, this would preclude their presence in the deposited SiO_2 leaving only C as the major impurity element.

The respective electrical characteristics monitored through capacitance measurements on MIM structures, with (a) Ga FIB deposited SiO_2, and (b) Xe FIB deposited SiO_2 as the insulator/dielectric are shown in Figure 4(b), where the C_{MIM} has been plotted with respect to C atomic %. For comparison and calibration, the capacitance/unit area $= \frac{\varepsilon_o \varepsilon_r}{t}$ of stoichiometric SiO_2 with a relative dielectric permittivity, ε_r of 3.9 (with ε_o being the vacuum permittivity



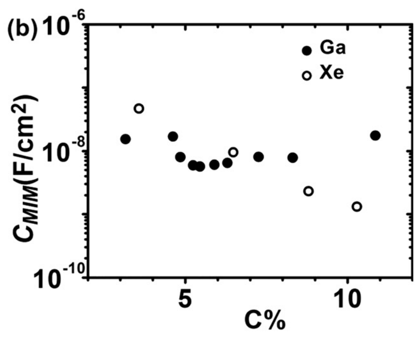


FIG. 4. The change of (a) the phase shift (θ) with Ga concentration using Ga ion based FIB depositions. (b) The capacitance per unit area of the *MIM* (*M*etal—FIB SiO_2 *I*nsulator—*M*etal) structures (C_{MIM}) with C concentration for both Ga and Xe ion FIB based SiO_2 deposition.

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of 8.854×10^{-12} C^2/Nm^2) for a 0.75 μm film thickness (t) (from Figure 1(b)), would be $\sim$4.6 nF/cm^2. For Ga FIB deposited SiO_2, the C_{MIM} was seen to be relatively constant at $\sim$10 nF/cm^2. The source of the capacitance was ascribed to the presence of the Ga^+ ions, inducing enhanced polarization through oxygen-ion binding.[22–24] However, with Xe FIB deposited SiO_2, there was an overall C_{MIM} decrease from $\sim$50 nF/cm^2 to $\sim$1 nF/cm^2. A tentative explanation of the capacitance decrease may be due to an effective reduction of the ε_r due to the C impurity. It was hypothesized[25] that C replaces some of the Si-O bonds (with bond energy $\sim$4.7 eV) in the SiO_2 forming Si-C bonds (with bond energy $\sim$3.5 eV).[26,27] An alternate and equivalent explanation is related to the Pauling electronegativity (EN) values of the Si, C, and O of 1.9, 2.6, and 3.4, respectively.[28] Given the difference in the EN, Si-C would be less polar than Si-O with a consequent[29] reduced ε_r and C_{MIM}.

IV. CONCLUSIONS

The ρ of SiO_2 deposited through the decomposition of organosilicate precursors in a Ga^+ based FIB was found to be orders of magnitude lower than that expected for high quality insulators. Metallic Ga, derived from the ion beam, was posited to be the source of the oxide contamination and the decreased ρ. A generalized two-constituent effective medium theory, where low resistivity Ga percolated through the FIB deposit matrix, was used to obtain agreement with data. However, an increasing carbon content also decreased the ρ of the oxide. A comparison of the electrical capacitance of the SiO_2 deposited through a Ga^+ ion based FIB with the oxide deposited using a Ga^+ free Xe based FIB system was made. A relatively constant capacitance with respect to increasing carbon content was recorded in the former case and ascribed to the Ga ions. It was also seen that the capacitance diminished with increasing carbon in the oxide deposited using the Ga^+ free FIB system, and was related to an effective reduction of the ε_r due to the formation of Si-C bonds. It can be concluded that Ga and C impurities, induced in FIB deposition, preclude the obtaining of high resistivity SiO_2 for interconnect isolation.

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[30] See supplementary material at http://dx.doi.org/10.1063/1.4902521 for (i) a listing of the various FIB parameters used to obtain the used O/Si, Ga, C values, and (ii) the sensitivity analysis of the relative roles of Ga and C.

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