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Citation: *Appl. Phys. Lett.* **110**, 074103 (2017); doi: 10.1063/1.4976311

View online: <http://dx.doi.org/10.1063/1.4976311>

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Water soluble nano-scale transient material germanium oxide for zero toxic waste based environmentally benign nano-manufacturing

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(Received 4 December 2016; accepted 25 January 2017; published online 14 February 2017)

In the recent past, with the advent of transient electronics for mostly implantable and secured electronic applications, the whole field effect transistor structure has been dissolved in a variety of chemicals. Here, we show simple water soluble nano-scale (sub-10 nm) germanium oxide (GeO₂) as the dissolvable component to remove the functional structures of metal oxide semiconductor devices and then reuse the expensive germanium substrate again for functional device fabrication. This way, in addition to transiency, we also show an environmentally friendly manufacturing process for a complementary metal oxide semiconductor (CMOS) technology. Every year, trillions of complementary metal oxide semiconductor (CMOS) electronics are manufactured and billions are disposed, which extend the harmful impact to our environment. Therefore, this is a key study to show a pragmatic approach for water soluble high performance electronics for environmentally friendly manufacturing and bioresorbable electronic applications. *Published by AIP Publishing.*
[\[http://dx.doi.org/10.1063/1.4976311\]](http://dx.doi.org/10.1063/1.4976311)

Transient electronics have received growing attention recently owing to its dissolvability for implantable and secured electronic applications.^{1,2} In these examples, the whole structure is dissolved over the time in a variety of chemicals. Here, we show that water soluble germanium dioxide (GeO₂) can be employed as a transient material besides its function as a dielectric layer. The usage of GeO₂ as the dissolvable material will still remove the key structure to serve the purpose of dissolution. At the same time, since it is simply water soluble, we can reuse the expensive germanium (Ge) substrate for further device fabrication.

GeO₂ can have three forms, two of them are crystalline and the third one is vitreous. Crystalline forms are represented by hexagonal and tetragonal crystalline structures.³ The growth conditions determine the resultant form of GeO₂, and the difference between them was reported by Johnson.⁴ Only hexagonal and vitreous form is water soluble. The hydrolysis mechanism of GeO₂ undergoes the following chemical reaction:⁵

Surface oxidation of Ge has been considered as an undesirable feature, which prevents Ge to be incorporated in the Complementary Metal Oxide Semiconductor (CMOS) industry for a long time. However, many studies have addressed a surface passivation challenge for the purpose of making use of superior material properties of Ge. Ge possesses favorable

properties such as high carrier mobility (up to 3900 cm² V⁻¹ s⁻¹ for electrons and 1900 cm² V⁻¹ s⁻¹ for holes),⁶ direct and small energy band gap (0.66 eV), small optical band gap (wide absorption wavelength spectrum), and low dopant thermal activation energies in comparison with the universal CMOS material Silicon (Si).⁷ As a result of unique properties, Ge becomes the material of choice for manufacturing high speed, low power devices,⁸ as well as optoelectronic devices.⁹

In this work, water soluble GeO₂ is a hallmark since it serves two different purposes as it allows for both recycling the substrate and reducing the pollution originated from discarded consumer electronics. We show that it would be of great benefit to meet the rapid growth demands for consumer electronics and keeping the electronic waste at bay simultaneously. Electronic waste is reported to be up to 42 × 10⁶ tons yearly.¹⁰ Moreover, water as an etchant of GeO₂ is highly preferable to other wet reactive chemicals as water is used frequently in the IC fabrication process for cleaning and etching purposes because: (i) it does not have an environmental impact, (ii) it is safe to handle easily, and (iii) it is relatively of low-cost.¹¹ On the other hand, the Ge/GeO₂ interface has a variety of satisfactory properties such as acceptable dielectric constant ($\kappa = 2.8$),¹² moderate refractive index, and adequate thermal stability.¹³ Besides that, GeO₂ has the advantage of suppressing the Ge dangling bond at the surface, which in turn minimizes the interface trap density.¹⁴

In this study, Metal Oxide Semiconductor Capacitors (MOSCAPs) are built on p-type Ge substrates using GeO₂ as

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a dielectric layer. After characterizing the capacitors, the substrate is rinsed with tap water in order to dissolve GeO_2 , which in turn takes away all the top layers. The substrate is then effectively reused to build the similar MOSCAPs again. GeO_2 is thermally grown on a p-type Ge (Ga-doped) $175\ \mu\text{m}$ thick substrate with resistivity ranging from 0.01 to $0.05\ \Omega\ \text{cm}$.

We start with 4-in. Ge wafer, which is then diced up to $2 \times 2\ \text{cm}^2$ experimental samples. Then, the pieces are cleaned with HF (49%), rinsed with Deionized (DI) water, blown dried in Nitrogen (N_2), followed by acetone and isopropanol based cleaning, and blown dried in N_2 . After that, the processed experimental samples are transferred into an Ultra High Vacuum Chemical Vapor Deposition (UHVCVD) chamber in order to grow GeO_2 . The chamber's temperature is stabilized at 400°C for 4 h in Oxygen (O_2) ambient with a flow rate of 100 sccm.

X-ray Photoemission Spectroscopy (XPS) was used to verify the substrate surface properties for a clean Ge surface, grown GeO_2 layer, GeO_2 removal, and regrown GeO_2 layer as it is capable to provide the chemical composition.¹⁵ XPS experiments were performed on a KRATOS Analytical AMICUS instrument equipped with an achromatic Al K α X-ray source (1468.6 eV). Typically, the source was operated at a voltage of 10 kV and a current of 10 mA. The pressure in the analysis chamber was below $4 \times 10^{-6}\ \text{Pa}$. In XPS, it is well known that $2p_{3/2}$ and $3d_{5/2}$ photoemission lines of the elemental Ge are detected at 1217.3 eV and 29.3 eV, respectively, and any peak shift in the binding energy is related to altering the oxidation state of Ge. XPS data recorded for a clean germanium sample and for the processed samples are compared in Fig. 1(a). The three processed samples refer to post GeO_2 growth (GeO_2 grown on pristine Ge after cleaning), post GeO_2 removal, and post GeO_2 re-growth

(GeO_2 grown after the first GeO_2 has been removed). XPS peaks of GeO_2 grown and GeO_2 regrown samples are identical and reveal a clear shift with respect to the reference sample. Indeed, the $2p_{3/2}$ and $3d_{5/2}$ photoemission lines are shifted by 2.8 eV and 3.5 eV, respectively, toward higher binding energy, which is specified to the fourth oxidation state (Ge^{+4}) of Ge and confirms the existence of the GeO_2 layer.^{7,13,16,17} However, the spectrum acquired for the reference germanium substrate is very similar to the one belonging to the rinsed sample, suggesting that both layers have the same composition. The quantitative data indicate that the reference and rinsed samples are composed of almost 50% of germanium and 50% of oxygen, whereas the grown and regrown layers contain 67% of oxygen and 33% of germanium. Precisely speaking, the major components of Ge $2p_{3/2}$ and Ge $3d_{5/2}$ of the reference and rinsed samples are detected, respectively, at 1218 eV and 29.6 eV. These values can be assigned to metallic germanium Ge.^{7,13,16,17} The smaller component detected mainly for Ge $2p_{3/2}$ at 1219.8 eV can be assigned to germanium monoxide (GeO). Hence, the most probable chemical composition of both reference and rinsed layers can be described by a thin over layer of native germanium monoxide (GeO) covering the metallic germanium. In contrast, the major components of Ge $2p_{3/2}$ and Ge $3d_{5/2}$ of the grown and regrown samples are detected, respectively, at 1221.2 eV and 32.8 eV. These values can be clearly assigned to germanium dioxide GeO_2 .^{7,13,16,17} The intensity of the Ge 3d component measured at 29.3 eV for the regrown layer is slightly higher than that measured for the grown one, suggesting that the regrown GeO_2 layer is thinner.

Knowledge of the Ge/ GeO_2 interface is essential for evaluating the quality of the growth method. A valuable insight into the Ge/ GeO_2 interface is obtained from TEM

FIG. 1. (a) High resolution XPS spectra of Ge 2p and Ge 3d peaks acquired for the reference Ge substrate, for the grown GeO_2 layer, for the same layer after submerging into tap water for 3 days, and for the re-grown GeO_2 layer after water based removal. (b) and (c) TEM images of GeO_2 for post-growth and post-re-growth samples, respectively. (d) and (e) AFM images of grown and regrown GeO_2 layers, respectively. (f) Thickness variation of GeO_2 across $10.76\ \text{mm}^2$ by spectroscopic ellipsometry. (g) Refraction index and extinction coefficient of GeO_2 .

images (Figs. 1(b) and 1(c)), which show a discontinuity free GeO_2 layer with a clear and slightly zig zag Ge/GeO_2 interface in both cases of post GeO_2 growth and post-regrowth GeO_2 samples. However, the surface of the Ge substrate becomes rougher after regrown GeO_2 and that introduces pronounced variation in the GeO_2 thickness. Atomic force microscopy (AFM) is employed to obtain the topographic imaging of $400\text{ }\mu\text{m}^2$ surface area of GeO_2 (Figs. 1(d) and 1(e)) and the RMS roughness found to be 1.89 nm and 5 nm for post GeO_2 growth and post-regrowth GeO_2 , respectively. The thickness uniformity of the thermally grown GeO_2 layer is examined using spectroscopic ellipsometry. The map of the scanned area of 10.76 mm^2 reveals uniform growth of germanium dioxide with an average thickness of $7.2 \pm 0.3\text{ nm}$ variation across the scanned area (Fig. 1(f)). The optical constants representing the refraction index (n) and extinction coefficient (K) of the GeO_2 layer have been measured and depicted in Fig. 1(g). A couple of features of this plot are worth pointing out. First, the measured refractive index at 550 nm is equal to 1.6, which is in total agreement with the reported value in previous studies.^{13,18} Furthermore, the maximum value of the extinction coefficient (K) of GeO_2 is observed at 246 nm, which means that GeO_2 has a tendency to be highly absorbing at 246 nm.

In order to get accurate information about the dissolution rate of GeO_2 , Emission-spectrometric detection of the elements at the ultra-trace level using inductively coupled plasma optical emission spectrometry (ICP-OES) is hired. The dissolution rate is systematically studied at different temperatures within the range of $T = 23\text{ }^\circ\text{C}$ and $T = 70\text{ }^\circ\text{C}$ for tap water, DI water, and Phosphate Buffered Solutions (PBS). The GeO_2 is thermally grown on p-type Ge pieces that have the same size ($1 \times 1\text{ cm}^2$). Then, every piece is submerged into 100 ml of a solution in a sealed Teflon bottle, which is placed in a thermal water bath at steady

temperature. Later, 5 ml of the solution is drawn every couple of hours and used to measure the concentration of Ge ions. In more detail, the solution is fed into a 50-MHz radio frequency (RF) induced argon plasma chamber from sample introduction nebulization systems, which is exposed to an elevated temperature up to approximately 7000–8000 K. At such atmosphere, all the analyte species are thermally excited through collisional excitation within the plasma. A photon at quantized energy is released when the atomic and ionic excited state species relax to the ground state, which in turn is used to identify the analyte species from which they originated. The concentration of the analyte species is directly proportional to the total number of photons.¹⁹ The detected wavelengths are equal to 219.871 nm, 204.377 nm, 259.253 nm, 209.426 nm, 265.117 nm, and 206.866 nm, which is certainly a fingerprint of Ge ions.²⁰ This demonstrates the removal of GeO_2 by dissolution with well-defined kinetics. The concentration of Ge ions is measured for all stipulated wavelengths. Then, the average of the concentration is plotted as a function of time (Figs. 2(a)–2(c)). The slope of solubility curves in linear regimes represents the dissolution rate of GeO_2 . The dissolution rate of GeO_2 is plotted at different temperatures for tap water, DI water, and PBS solution as depicted in Fig. 2(d). Fig. 2(d) sheds some light on the dissolution rate of GeO_2 from different aspects. First of all, there is a highly significant distinction between the dissolution rate of GeO_2 in tap water on one side and DI water and PBS solutions on the other side. Further, the dissolution rate of GeO_2 increases remarkably with temperature in tap water, whereas it increases slightly in DI water and PBS solutions, as well. As a result, the dissolution rate of GeO_2 could be controlled based on the temperature and pH values of the solution. From the chemistry point of view, the three solutions used in this study differ from each other in the pH value. The tap water has the highest pH value (8.9) among

FIG. 2. (a)–(c) Concentration of Ge ions measured by (ICP-OES). (b) Dissolution rate of GeO_2 .

other employed solutions and has a clear impact on speeding up the dissolution rate of GeO_2 (Fig. 2(d)). The pH value indicates that tap water has a higher relative number of hydroxyl ions (OH^-) in comparison to DI water (pH = 6.6) and PBS (pH = 7.4). OH^- ions are of great importance to initiate the hydrolysis reaction of GeO_2 with water. Strictly speaking, the physical properties, in particular, the ionic charge z and the ionic radius of the material, will determine under which pH value will the material hydrolyze.²¹ Additionally, the presence of OH^- ion in the solution will speed up the hydrolysis reaction because the reactivity of OH^- ions is four orders of magnitude greater than H_2O .²² In future, the scope of the influence of pH needs to be studied in more detail. On the other hand, the solution's temperature can accelerate the dissolution rate, which can be explained based on the kinetic molecular theory and the temperature dependence of reaction rate constant, which in turn quantifies the rate of a chemical reaction.²³

MOSCAPs (with area $2.19 \times 10^{-4} \text{ mm}^2$) are fabricated in order to study the utility of GeO_2 as a dielectric layer in the case of post GeO_2 growth and post-regrowth samples. The process flow starts with the Ge substrate that is first diced to $2 \times 2 \text{ cm}^2$ pieces and cleaned with acetone and isopropanol. Then, Ti (40 nm)/Pt (60 nm) is sputtered in the backside to serve as a back electrode and to prevent GeO_2 from growing on the backside of the pieces. Then, GeO_2 is grown. Later on, sputtered Al (250 nm) is patterned through a shadow mask to serve as a gate electrode Fig. 3(a). The data of CV measurement were collected by an LCR meter at 1 MHz. After characterizing the MOS capacitors, the piece is immersed into a tap water at RT and sonicated for 60 min every 24 h for three days with replacing the water daily. The dissolution of the GeO_2 layer starts at the exposed area and at the edge of the Al patterned layer, which in turn facilitates removing the Al layer (Fig. 3(b)). Then, the pieces were examined by XPS to verify the absence of GeO_2 . Later, the piece is treated exactly as the first time in order to clean it and rebuild the MOSCAPs. The C-V characteristics of capacitors in both cases (post GeO_2 growth and post-regrowth samples)

are shown in Fig. 3(c). For the first-time growth sample, we notice a capacitance value of 495 pF for devices. For the purpose of extracting the value of dielectric constant of the GeO_2 layer, the universal equation is employed

$$C = \frac{\kappa \epsilon_0 A}{d}, \quad (2)$$

where κ is the dielectric constant, ϵ_0 is the vacuum permittivity, A is the device area, and d is the dielectric thickness. According to the thickness scan map shown in Fig. 1(f), the d value of 7.2 nm has been chosen for the calculation of κ . The calculated value came to be ~ 1.84 , which is consistent with the previous literature,¹⁸ showing similar dielectric properties as shown from ellipsometry data, Figs. 1(g) and 3(d), where the increase in the dielectric constant for photon energies larger than 3 eV is attributed to sub-bandgap photo-absorption due to significant density of gap states. The existence of mid-gap states could also explain the bump shown in the CV curve in Fig. 3(c).²⁴ After the regrowth of the GeO_2 layer, the oxide capacitance becomes 43% higher than the original value. Spectroscopic ellipsometry data (Fig. 3(d)) have shown the dielectric constant of the regrown sample to be identical to that of the first-time growth. Therefore, using the extracted dielectric constant from the first growth capacitance measurement, 1.84, we extracted a dielectric thickness of $\sim 5 \text{ nm}$ and this was confirmed by the spectroscopic ellipsometry measurement. This proves that the thickness reduction of GeO_2 is behind the 43% higher capacitance after regrowth. We have independently calculated the dielectric constant using the C-V measurements and measured film thicknesses for post-growth and post-regrowth samples, which yielded a similar dielectric constant (Figure S1 in the supplementary material).

We have shown how water soluble sub-10 nm GeO_2 can be effectively used for environmentally benign zero toxic waste CMOS manufacturing for scaled high performance CMOS electronics, transient electronics for water solvable low-cost transient sensory systems.

FIG. 3. (a) Fabrication flow of MOS capacitors. (b) Chronological optical images gathered at different stages of dissolution of GeO_2 (0–3 days). (c) CV measurement of MOS capacitors at 1 MHz for post-growth and post regrowth GeO_2 samples. (d) Dielectric constant of GeO_2 post-growth and post-regrowth.

See [supplementary material](#) for extracting the relative dielectric constant κ from CV measurement and atomic force microscopy of GeO₂ after immersed in tap water. Two figures (Figs. S1 and S2) are also included.

This publication is based on the work supported by the King Abdullah University of Science and Technology (KAUST).

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