Giant Conductivity Modulation of Aluminum Oxide using Focused Ion Beam

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Precise control of the conductivity of semiconductors through doping has enabled the creation of advanced electronic devices, similarly, the ability to control the conductivity in oxides can enable novel advanced electronic and optoelectronic functionalities. While this was successfully shown for moderately insulating oxides, such as In₂O₃, a reliable method for increasing the conductivity of highly insulating, wide bandgap dielectrics, such as aluminum oxide (Al₂O₃), has not been reported yet. Al₂O₃ is a material of significant technological interest, permeating diverse fields of application, thanks to its exceptional mechanical strength and dielectric properties.

Here we present a versatile method for precisely changing the conductivity of Al₂O₃. Our approach greatly exceeds the magnitude of the best previously reported change of conductivity in an oxide (In₂O₃). With an increase in conductivity of about 14 orders of magnitude, our method presents about 10 orders of magnitude higher change in conductivity than the best previously reported result. Our method can use focused ion beam to produce conductive zones with nanoscale resolution within the insulating Al₂O₃ matrix. We investigated the source of conductivity modulation and identified trap-assisted conduction in the ion damage-induced defects as the main charge transport mechanism. Temperature-dependency of the conductivity and optical characterization of the patterned areas offer further insight into the nature of the conduction mechanism. We also show that the process is extremely reproducible and robust against moderate annealing temperatures and chemical environment.

The record conductivity modulation, combined with the nanoscale patterning precision allows the creation of conductive zones within a highly insulating, mechanically hard, chemically inert, and bio-compatible matrix, which could find broad applications in electronics, optoelectronics, and medical implants.

Aluminum oxide (Al₂O₃) is one of the most widely employed dielectric materials, thanks to its excellent insulating properties, mechanical hardness and resistance, and biocompatibility, with applications ranging from device passivation, MOSFET gate, to biomedical implants and antifouling passivation. Electrical functionalization of Al₂O₃ via reliable and spatially-accurate control of its conductivity could enable novel sensing technologies encompassing electrical contacts embedded in a mechanically hard, chemically inert, and electrically insulating dielectric matrix. Examples of such technological applications include photon emission and detection, low-energy ion beam passivation, energy conversion, and implantable devices.

We here present an effective method for the non-subtractive nanopatterning of electrically conductive wires and other features embedded in a dielectric Al₂O₃ substrate, using focused ion beam (FIB). While patterning of nanowires in transparent conductive In₂O₃ has been demonstrated using FIB, the conductivity modulation was limited to 4 orders of magnitude. Here, we show nanopatterning of conductive zones in highly insulating Al₂O₃, achieving a conductivity modulation of 14 orders of magnitude (see Supporting Information). To the best of our knowledge, this is the highest reported change in conductivity using FIB.

FIB has proven to be an extremely effective tool for the nanopatterning of transparent conducting oxides (TCO) via lithographically controlled dopant implantation, as well as for structural modification and non-subtractive patterning of dielectric substrates. Despite being an inherently serial processing tool, FIB has shown very attractive potential in large-area milling and implantation, in particular when integrated with pattern generator lithography capabilities. Furthermore, thanks to the higher beam deflection speed and lower settling time compared to electron beams, milling-based ion beam lithography (IBL) has demonstrated exposure times for large patterns that are comparable to those of EBL, and even faster patterning times can be achieved for ion implantation at lower dosage.

Methods

The process schematic of our method is presented in Figure 1: the fabrication process is fairly simple, highly tunable, extremely versatile, and can be applied to both bulk Al₂O₃ (i.e., sapphire) and thin film Al₂O₃ (e.g., ALD). In order to limit the effects of charging, inherent to FIB processing of insulating substrates, a metallic alignment pattern is deposited on the sample before implantation using lithographic techniques (Figure 1a). This metallic film serves a dual purpose: it is connected to ground during implantation, allowing to avoid excessive charging of the substrate, and facilitates the focusing and alignment of the ion beam, crucial for the subsequent processing steps. Alternatively, in order to further improve the spatial resolution of the patterned nanowires, an anticharging thin layer of Au can be deposited over the whole area of the sample before implantation, and subsequently removed, as proposed by Sosa et al.

All the implanted wire-like structures exhibit ohmic behav-
Defect-assisted conduction.

Device Characterization

Defect-assisted conduction. Several theoretical and experimental studies have advanced the hypothesis that damage-induced defects in electronic materials can create deep trap states in the bandgap, which intrinsically act as dopants, enabling electrical conduction in otherwise highly insulating materials. These studies suggest that the electrical conductivity we observe in Al₂O₃ could be due to the formation of oxygen vacancies caused by the ion collision cascade. To evaluate this hypothesis, we performed an annealing study as it was proved to be an effective tool for investigating the nature of the electrical conductivity in implanted wires in TCO.

The results of rapid thermal annealing (RTA) treatment is presented in Figure 2c. Annealing at 750°C in an oxidizing environment effectively erases the implanted wire, reducing the electrical conductivity to negligible levels, while annealing in a reducing environment (N₂) induces a higher conductivity in both the implanted wires and the non-implanted Al₂O₃ matrix. RTA treatments performed at 500°C result in a slight decrease in conductivity in both chemical environments, presumably due to incomplete activation of the defect annealing at such temperature. These results are consistent with published results for RTA treatment of implanted Ga nanowires in In₂O₃, and suggest that the electrical conductivity of the patterned wires is related to ion damage-induced chemical and structural modification of the Al₂O₃ matrix, rather than to the implanted Ga ions.

Charge transport. To further evaluate the nature of the charge transport mechanism, we performed temperature-dependent conductivity characterization of the implanted devices. Figure 2d reveals a decrease in conductivity with the inverse of temperature. Transport in a wide bandgap dielectric such as Al₂O₃ is governed by hopping conduction mechanisms of two types: direct trap-to-trap tunneling, and phonon-assisted elastic and inelastic tunneling. For both conduction mechanisms, temperature affects the density of free carriers, due to the thermal excitation of electrons at the trap sites, and the carrier mobility, due to the thermally activated phonon scattering. Therefore, the temperature dependency of the conductivity \( \sigma = \eta q \mu \) can be modeled as

\[
\sigma = \alpha T^{-3/2} e^{-E_{ACT} / k_B T}
\]

where \( \alpha \) is a fitting parameter, \( k_B \) is Boltzmann’s constant and \( E_{ACT} \) is the activation energy in units of electron-Volt.
Within the range of temperatures investigated, two conduction regimes are observed: one dominated by thermally activated phonons, at higher temperatures ($T > 200\,K$), and one by direct hopping at lower temperatures; hence a good fit to the experimental data ($R^2 = 0.994$) is only possible by adding two functions of the form of eq. 1, with estimated activation energies of 96 meV and 50 meV.

**Optical characterization.** We also evaluated the effect of the implantation on the optical properties of the sapphire substrate. Figure 3 shows a significant change in the photoluminescence (PL) and transmission spectra of implanted samples compared to the pristine sapphire. These measurements supporting the argument for the ion damage-induced formation of trap states within the oxide bandgap. While the change in both PL and transmission due to implantation spans over a large range of wavelengths, interestingly, the characteristic $Cr^{3+}$ impurity peak shown in Figure 3b is unaffected by the implantation process, hence suggesting a wider energy distribution of trap states in the bandgap, as compared to atomic transition levels.

**Conclusion**

We reported a novel method for nanopatterning of conductive zones in Al$_2$O$_3$ matrix using focused ion beam irradiation. The implanted wires exhibit ohmic conduction with an average conductivity of $10^{-2} \, S cm^{-1}$. Based on a large number of measured devices, we showed that the presented nanopatterning process has excellent uniformity and nanoscale spatial resolution, while allowing for modulation of the electrical conductivity through control of the ion dose. The electrical, optical, and chemical characterizations provide strong evidence that the conduction mechanism is due to the formation of trap states within the oxide bandgap. All processed devices showed stable performance during several months, and after heating to 100°C and immersion in liquid solvents. The present method shows great potential for application in sensing technologies that require electrical contacts embedded in a mechanically hard, chemically inert, and electrically insulating dielectric matrix. Examples of such applications include photon sensors, low-energy interconnects, and micro/nano-implantable medical devices.

**Experimental**

The majority of the devices presented were implanted in a 300 μm thick, double-side polished <0001> crystalline sapphire substrates. Some of the devices were implanted in an Al$_2$O$_3$ film deposited on both silicon and sapphire substrate using a Cambridge NanoTech Savannah S100 atomic layer deposition from Trimethylaluminum and water vapor precursors at 150°C. An 80 nm Cu layer with alignment mark pattern was deposited on the sample before implantation using photolithographic lift-off techniques. The metallic layer was connected to ground during implantation. A FEI Nova 600...
NanoLab dual-beam microscope with a Sidewinder Ga+ ion column and a 100 nm resolution piezomotor X-Y stage was employed for the wire implantation at ion beam energies of 5 and 30 keV and currents of 100 pA, 3.2 and 6.3 nA, yielding estimated spot sizes ranging 20 to 60 nm. The instrument was combined with a RAITH Elphy 4.0 interface with integrated 16-bit DAC pattern generator, which enables large area patterning and write-field alignment, accounting for stitching and drift, and allows for precise dose control via beam blank and deflection. The Elphy interface allows for a multi-pass patterning technique, which help contrast the strong charging in dielectrics. Nevertheless, we estimate the effective dose to be lower than the nominal value, due to sputtering and localized charging deflecting the incident ions. The Ti/Au contacts were subsequently deposited with photolithographic lift-off techniques, and electrical testing was performed with a 4-point probe station equipped with Agilent 4285A LCR meter. Photoluminescence spectra were acquired using a HORIBA LabRAM HR Evolution confocal Raman, equipped with 473 nm, 532 nm, 633 nm and 785 nm lasers for excitation.

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AUTHOR CONTRIBUTIONS
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COMPETING FINANCIAL INTERESTS
The authors declare no competing financial interests.

SUPPORTING INFORMATION
The following supporting information is available from the author:

Table S1: Calculations of magnitude conductivity modulation in Al₂O₃ reported in this paper compared to that previously reported for In₂O₃.²⁸,²⁹,³⁸

Figure S1: Additional proof for uniformity of the implanted conductive regions after RTA treatments

Figure S2: Additional graphic visualization of current-voltage characteristics after RTA treatments

Table S2: Complete set of current-voltage measurements performed on all the fabricated devices

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