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Stable, low-resistance, 1.5 to 3.5 k Ω sq⁻¹, diamond surface conduction with a mixed metal-oxide protective film



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ABSTRACT

Semiconducting diamond has the potential for an order-of-magnitude increase in power handling over currently used semiconductors. This is made possible by diamond's higher thermal conductivity and a higher breakdown voltage than any other device-quality semiconductor. Diamond power devices have numerous potential applications in the power grid and in high-power high-frequency RF applications.

One approach to leverage diamond's abilities is through the fabrication of field-effect transistors (FETs). The FET is made by forming a p-type surface conductive layer on the diamond surface. This is accomplished by terminating the diamond surface with hydrogen atoms and then coating the surface with a material that contains negative charges to compensate for the positive holes in the p-type layer. Impressive drain current (1.3 A mm⁻¹), maximum operational voltages (> 2000 V), and frequencies of unity current gain (f_T of 75 GHz) have been demonstrated with this surface conductance method. This surface layer, however, is not stable and FET performance degrades over time on the scale of hours to days. This paper describes an encapsulating layer with a mixed oxide, Al₂O₃-SiO₂, which maintains the resistance of the conductive layer in the range of 1.5 to 3.5 k Ω sq.⁻¹ by protecting the diamond surface while maintaining a stable negative charge.

1. Introduction

Semiconducting diamond with its high thermal conductivity and high breakdown electric field has the potential for a significant increase in power handling over present devices [1] once several technical challenges are overcome. When the surface of diamond is H-terminated, a p-type surface conductive layer is formed. Atmospheric impurities such as NO₂, O₃ [2–4], fluoropolymer [5] and Al₂O₃ [6] adhere to the diamond surface and activate diamond's surface conductance by generating and trapping negative charges on the diamond surface. This generation of holes in the diamond by a surface coating is called transfer doping. These charges increase the positive p-type carrier density in the diamond surface and reduce its resistance. High-drain current field-effect transistors (FETs) of 1.2 to 1.3 A mm⁻¹ [5–7], high frequency (f_T of 75 GHz [8]), and high voltage (2000 V [9]) devices have been demonstrated with these activation surface chemistries. However, these devices degraded in a few days or when stressed [8,10].

Research to stabilize diamond's surface conductance has found some success. H-terminated (100)-oriented diamonds coated with Al₂O₃ using atomic layer deposition (ALD) have the best demonstrated stability, but the surface resistance is high (5 to 12 k Ω sq.⁻¹) [6,10]. Diamonds coated with transition metal oxides such as WO₃, MoO₃, and V₂O₅ have lower resistances of 1 to 7 k Ω sq.⁻¹ [11–15] and their

stability has been demonstrated [11,15]. However, these oxides are used for electrochromic displays because they are conductive, have several oxidation states with different transparencies and colors [16]. These properties may degrade FET performance under the high electric fields associated with FETs. This article will discuss the use of a mixed-oxide (Al₂O₃-SiO₂) ALD film to generate surface resistances between 1.5 and 3.5 k Ω sq.⁻¹ with demonstrated stability in excess of half a year.

2. Theory and previous efforts

The activation of the H-terminated diamond surface by adsorbed gases or by overcoating with Al_2O_3 or transition metal oxides, WO_3 , is the result of empty electron states below diamond's valence band maximum (VBM), as depicted in Fig. 1. These states capture electrons from the diamond and generate holes that make the diamond surface conductive. The energy difference, ΔE , between diamond's VBM and these states is one parameter determining the level of surface conductance.

 ΔE is often measured in units of electron volts (eV), but can also be characterized by the effective acid character of the overlayer. Levy [17] calculated that for a pH < 4.0 the acid character of the overlayer will generate holes in diamond and form a conductive layer.

Since the 1940's, mixed oxides such as SiO_2 , Al_2O_3 , TiO_2 , ZrO_2 are

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Fig. 1. Schematic drawings of diamond's energy levels and the chemistry on the diamond surface. (a) An example where adsorbed chemicals in the atmosphere have electron affinities below that of diamond's valence band maximum (VBM) and form negative ions and mobile positive charges, holes, in the diamond. (b) An example of transition-metal oxides, WO_3 , MO_3 , and V_2O_5 , with their conduction band minimum (CBM) below diamond's VBM. Electrons leave diamond's valence band for the oxide's conduction band forming valence band holes in the diamond. (c) An example of an inert material matrix that is doped with atoms or compounds that trap electrons from the diamond in a similar manner to (a) except the negative ions are stabilized by the matrix.



Fig. 2. Graph of the density of surface acid sites and their acid strength for several mixed metal oxides. An estimate of the energy below vacuum of the acid sites was obtained by assuming Eq. (1) is operating and by extending the interpretation of Hammett acidity to that of pH [22]. The work function of MoO_3 is shown for comparison. [a] Ref [19], [b] Ref [20], and [c] Ref [26].

used as catalysts in the oil industry to crack long chain paraffin molecules [18]. Their catalytic function is a result of their strong acid property. Fig. 2 shows several metal oxide catalysts with their Hammett acidity, H₀, and the surface density of these acid sites [19,20,26]. H₀ is an extension of the commonly used negative log of the hydrogen ion concentration, pH, extended to solvents other than H₂O and for acids with their effective pH < 1 [22]. H₀ and the density of surface acid sites on the mixed oxide surface was determined by pulverizing the mixed oxide into a powder. The powder is mixed with a liquid, like benzene, to form a slurry and the acidity is measured by adding acid indicator dyes to the slurry that change their color a specific H_0 . The acid site surface density was obtained by measuring the surface area of the powder using the BET method [23] and then titrating a base into the liquid slurry until the acid is neutralized [21,24]. The actual character of the mixed oxides varies depending upon how they are generated from their starting oxides and we have not measured the acidity of our ALD films.

Fig. 2 also shows estimates of the electromotive potential for these acids assuming the overall chemical reaction between the diamond surface and the H^+ from the acid is [25]:

$$2\text{Diamond} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \ge 2\text{Diamond}^+ + \text{H}_2\text{O}$$
(1)

Another acid-driven chemical reaction without oxygen is.

Diamond + $H^+ \ge Diamond^+ + \frac{1}{2}H_2$

(2)

The reaction in Eq. (2) has an electromotive potential 1.23 V less that than the reaction in Eq. (1). This means that the ability of these mixed oxides to generate a conductive layer in diamond is reduced without the presence of O_2 . In the presence of O_2 the oxide mixture, Al_2O_3 -SiO₂, has superior 6.45 eV electromotive potential [20] when compared with the work function of MoO₃ [26].

From Fig. 2 neither SiO₂ nor Al₂O₃ are strong acids or have a high density of surface states. However, Al₂O₃-SiO₂ is a strong acid and has a high density of surface states, making it a candidate for activating the surface conduction of diamond. Several groups have modeled Al₂O₃-SiO₂ [27–29] and believe the key to the acid character is that the Al atom can be substituted for a Si in the SiO₂ matrix where it is surrounded by four O atoms, a tetrahedral site. The Al atom with a valence



Fig. 3. One of several models of the acid properties of Al_2O_3 -SiO₂ favored by Awakamis et al. [29]. The surface acid site is the Si⁺OH₂ \Leftrightarrow SiOH +H⁺₁ acting as a Bronsted acid (a proton donor). The Al, acting as a Lewis acid (an electron acceptor), is in a tetrahedral site and acquires an electron from the surface Si.

state of three instead of silicon's four can acquire an extra electron to accommodate the SiO₂ structure. Fig. 3 shows a possible Al₂O₃-SiO₂ configuration by Awakamis et al. [29] that would generate an acidic property. Annealing the Al₂O₃-SiO₂ mixed oxide above 650 °C will cause the Al to move into an octahedral site, surrounded by eight O atoms and resulting in a change to the acidic properties of the Al₂O₃-SiO₂ [29].

3. Procedure

For the experiments reported here commercial CVD-grown (100)single crystal diamonds were used. The diamond were cleaned in H_2SO_4 - H_2O_2 and rinsed in water and acetone until no H_2SO_4 residue was present under optical microscopic examination. Alkali metal salts like NaNO₃ and KNO₃ were avoided. The diamonds were H-terminated (as described previously [30]) in a plasma system with an optical spectrometer to measure the impurities in the plasma. The system was cleaned prior to H termination in a hydrogen-oxygen plasma until optical emissions lines common to carbon contamination 387, 430, and 513 nm were no longer visible. Additionally, if optical emission lines indicating the presence of N at 335 and 355 nm, of Na at 590 nm, of K at 766 nm, or O at 308 nm were observed, the H termination was stopped and the source of these elements was removed. After termination the diamonds were either immediately covered in ALD oxides or stored in dry nitrogen until ALD was available.

ALD is a comparatively new technology to deposit submicron layers of metal oxides. Fig. 4 shows the ALD system used in these experiments with a load lock and an optical pyrometer. Several experiments were performed with the goal of depositing an acidic mixed oxide of SiO₂ and Al₂O₃. Previous experiments using a plasma of either H₂ or O₂ in this system destroys the surface conductance, so only H₂O was available as an oxidizer of the Al and Si precursors. The Al precursor is Al(CH₃)₃, TMA, and two Si sources were available, Si(N(CH₂CH₃)₄ (BDEA) and ((CH₃)₃CO)₃SiOH (TBS). Alternately depositing TMA and either BDEA or TBS with H₂O as the oxidizer did not result in a surface conductance < 5 kΩ sq.⁻¹. However, films made with alternate applications of TMA, TBS, and H₂O did generate a surface conductance ~2.3 kΩ sq.⁻¹ after a 600 °C anneal in forming gas, but bubbles formed between the diamond and the film after the anneal as reported by Karawada [10].

With the assumption that organic residue or the amine of BDEA in the ALD films might be compensating the Al_2O_3 -SiO₂ acid character,



Fig. 4. Photograph of the atomic layer deposition (ALD) system used in these experiments. The sample temperature was measured using an optical pyrometer, and calibrated with thermal melt powders. The system's load-lock allows for sample loading without venting the main chamber.



Fig. 5. Graph of the sample's temperature as a function of time. Four minutes after the sample is loaded ALD of Al_2O_3 is started.

another approach was taken. Instead of co-depositing Si and Al oxides, the ALD chamber and sample stage were first precoated at 350 °C with SiO₂ using BDEA and an O₂ plasma. The stage was then moved to the interlock and allowed to cool to room temperature. A hydrogen-terminated diamond was loaded into the interlock and transferred into the system. Once loaded, the sample stage and the diamond's temperature starts to increase from room temperature to 350 °C, which takes approximately 20 min. However, the deposition of Al₂O₃ starts with H₂O first and then TMA after 4 min when the diamond temperature is ~150 °C. Deposition continues for the next ~20 min to deposit a 20-nm film. The time-temperature history is shown in Fig. 5. After deposition the diamond is moved to the interlock and allowed to cool to room temperature before venting to air. Fig. 6 shows secondary ion mass spectrometry (SIMS) characterization of the ALD film. The SIMS data shows that Si is carried over from the previous run at a fraction of a percent of the Al concentration. The presence of Si carried over from the previous ALD run was also confirmed by x-ray photoelectron



Fig. 6. Secondary ion mass spectrometry, SIMS, for Si and C on two diamonds. Both diamonds were ALD coated with Al_2O_3 , one with the ALD system previously used to deposit SiO₂ and the other after the system deposited Al_2O_3 . The appearance of Si inside the diamond is believed to be due to variation in the thickness and sputtering rate of the ALD oxide film.



Fig. 7. Surface resistance as a function of time for three diamonds. All three were H-terminated. One was exposed to laboratory air and the other two were coated with Al_2O_3 -SiO₂ as described. One was placed in dry N_2 for 2.6 days and then exposed to air and the other was exposed to air after Al_2O_3 -SiO₂ deposition.

spectroscopy, XPS. The Si contribution to the acid character would be only in the first few atomic layers on the diamond surface where the Si concentration could be larger than the SIMS would indicate.

Once taken out of the ALD system, the surface resistance, measure with a van der Pauw method, is between 5 and 10 k Ω sq.⁻¹ and then decreases to 1.5 to 3.5 k Ω sq.⁻¹ over 1 to 3 days in laboratory air. The surface resistance remains in the high-resistance state if kept in dry N₂, shown in Fig. 7. Once in the low-resistance state, the surface resistance remains in this state for over 200 days, as shown in Fig. 8. Fig. 9 shows the Hall mobility and carrier density over the same 200-day period. The mobility decreases as the carrier density increases, resulting in nearly constant resistances. When the diamond is heated to 600 °C in forming gas or ashed in a He–O₂ plasma, the resistance again increases to ~10 k Ω sq.⁻¹ but recovers its low-resistance state in hours.

The purpose of this effort is to obtain a stable FET. Fig. 10 shows a comparison of two diamond metal-semiconductor field-effect transistors, MESFETs, fabricated in a manor outlined by Moran et al. [31] and described in more detail in the appendix. One is fabricated without a protective Al_2O_3 -SiO₂ film and the other is overcoated with 20 nm of Al_2O_3 -SiO₂. Although the drain current of the MESFET with Al_2O_3 -SiO₂ is lower, it is stable in time while the drain current of the unprotected MESFET decreases exponentially with a time constant of 1.2 days. Fig. 11 shows a typical drain current of an Al_2O_3 -SiO₂ overcoated MESFET as a function of drain voltage. The device contacts are also coated with the Al_2O_3 -SiO₂, but the probes easily break though this layer to the gold contacts.

For the surface resistances reported here once the diamond is H terminated it is either stored in dry N_2 or immediately overcoated with Al_2O_3 -SiO₂. However, for the devices shown here the FET is fabricated first before ALD of Al_2O_3 -SiO₂. It is very difficult to clean off the submonolayers of residual photoresist and chemical etchants used during fabrication and the resulting surface conductance is degraded by these impurities. At present our FET fabrication procedure compromises the surface conduction of the Al_2O_3 -SiO₂ diamond structure resulting in lower drain current than would be expected from the measured surface resistance before device processing.



Fig. 8. Comparison of the resistance of three diamonds all hydrogen terminated and in air as a function of time. One diamond was exposed to just air, another was exposed to NO₂ for \sim 1 min [30] and the third diamond was coated with ALD Al₂O₃-SiO₂ as discussed in text.



Fig. 9. The Hall mobility and carrier density as a function of time for the ALD coated diamond shown in Fig. 8 The decrease in mobility with time is offset by the increase in carrier density to give an also most constant surface resistance. The lines for mobility and carrier density are linear fits to the data.

4. Discussion

This article discusses one of a large class of mixed metal-oxide acids known since the 1940's. The acidic property appears with the mixed oxide matrix, while the individual oxides have little to no acidic character. These acids are able to increase the surface conduction of hydrogen-terminated diamond. Al₂O₃-SiO₂, the mixed oxide discussed here, is classified as a super acid, having an H₀ < -12 [33]. It both protects the diamond's surface and generates some of the lowest stable surface resistances to date.

Fig. 2 only shows binary-metal oxides. However, there also exist tri-



Fig. 10. Comparison of drain current for two metal-semiconductor field-effect transistors, MESFETs, as a function of time. One is uncoated and the other overcoated with ALD SiO₂-Al₂O₃, as described above. Both are exposed to air. The gate length is 400 nm and the source-drain length is 1 μ m [32].



Fig. 11. Drain current as a function of drain voltage for several gate biases of the MESFET passivated with ALD Al₂O₃-SiO₂ just before stressing, shown in Fig. 10. The drain current at $V_{drain} = -10$ V and $V_{gate} = -4$ v was 125 mA mm⁻¹, which increase to ~135 mA mm⁻¹ by the time the stress test was started.

metal-oxide acids as well as metal phosphates and sulfates many of which are reviewed by Corma [18]. With the recent advent of ALD technology most of these acids are accessible as thin films. The difficulty is in depositing them while still maintaining their acidic properties. This is especially difficult during FET fabrication when residual organics from photoresist and other sources coat the diamond surface and compromise ALD surface conductivity.

Air exposure after ALD is required to obtain the low surface

resistance. In nitrogen or argon, the resistance will remain high, > 3.5 k Ω sq.⁻¹. This is consistent with the chemical reaction of Eq. (1) where the presence of O₂ enhances the driving force to extract electrons out of the diamond. Whether the O₂ diffuses through the ALD film and H₂O diffuses out or H₂ diffuses to the ALD-air surface where it is oxidized remains an unanswered question. The transition metal oxides, which are believed to have no H₂-O₂ reaction also require a similar waiting period to obtain their low surface resistance [private communication with David Moran and Kevin Crawford]. In addition to the chemical reactions necessary for activating diamond with these mixed metal oxides, as discussed above, NO₂, O₃, and just the O₂ in air are known to remove H from the diamond surface and replace it with OH and other O groups [3,4,34]. Such limited chemical oxidation is known to enhance diamond's surface conductance and could also be happening with these mixed metal oxides and the transition metal oxides.

5. Conclusion

Taking care to minimize those impurities that compromise the quality of H termination, C, N, alkali metals, and O and overcoating the H terminated surface with an ALD Al₂O₃ layer doped with SiO₂, diamond surface resistances between 1.5 and 3.5 k Ω sq.⁻¹ were obtained. These are some of the lowest resistances reported for (100) oriented diamond. While unprotected H-terminated diamond surface resistance slowly increases over several days, once coated with Al₂O₃-SiO₂ the resistance is stable in air > 200 days. We speculate the low resistance is a result of the acid property of Al₂O₃-SiO₂, which is not present for the undoped ALD Al₂O₃.

CRediT authorship contribution statement

M.W. Geis: Conceptualization, Methodology, Software, Data curation, Writing - original draft. J.O. Varghese: Conceptualization, Methodology, Software, Data curation, Writing - original draft. M.A. Hollis: Conceptualization, Writing - review & editing. Y. Yichen: Resources. R.J. Nemanich: Resources. C.H. Wuorio: Resources. Xi Zhang: Conceptualization, Writing - review & editing. G.W. Turner: Conceptualization, Writing - review & editing. S.M. Warnock: Writing - review & editing. S.A. Vitale: Resources. R.J. Molnar: Resources. T. Osadchy: Resources. B. Zhang: Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: some of the technology discussed here is patented.

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Appendix

FET fabrication

Field-effect transistor devices were fabricated on single-crystal diamonds with (100) orientation. The diamond wafers were cleaned prior to fabrication using a mixture of H₂SO₄:H₂O₂ (2:1) for 30 min, then thoroughly rinsed with de-ionized water and blown dry with N₂. The diamond wafers were then H-terminated in a CVD plasma reactor (Seki) for 1 min at 850 deg. C. After H-termination the wafers were coated with 300 nm of gold. Devices were then patterned on the gold using photolithography and Transene gold etch. Gate contacts were fabricated using e-beam lithography to open areas over the channel regions of the devices, removing the gold layer using Transene gold etch, and finally evaporating aluminum, 100 nm thick. The devices were isolated using an oxygen plasma ash at 100 W for 1 min. This is a similar procedure to Moran's device fabrication procedure, D. A. J. Moran, O. J. L. Fox, H. McLelland, S. Russell, P. W. May. Scaling of hydrogen-terminated diamond FETs to sub-100-nm gate dimensions. IEEE Electr. Dev. Lett. 32 (2011) 599-601. DOI: 10.1109/ LED.2011.2114871

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