Surface Intensive Materials Processing for Multi-Functional Purposes

D. Ilia, E. K. Williams, C. I. Muntele, and M. A. George
Alabama A&M University
Normal, AL

D. B. Poker and D. K. Hensley
Oak Ridge National Laboratory
Oak Ridge, TN

D. J. Larkin
NASA Glenn Research Center
Cleveland, OH

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SURFACE INTENSIVE MATERIALS PROCESSING FOR MULTIFUNCTIONAL PURPOSES


a Center for Irradiation of Materials, Alabama A&M University, Normal, AL 35762, USA
b Dept. of Chemistry, University of Alabama in Huntsville, Huntsville, AL 35802, USA
c Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
d NASA Glenn Research Center, Cleveland, OH, 44135, USA

We have chosen silicon carbide (SiC) as a multi-functional material to demonstrate the application of surface intensive processing for device fabrication. We will highlight two devices which are produced in house at the Center for Irradiation of materials of Alabama A&M university: A) High temperature electronic gas sensor, B) High temperature optical properties/sensor.

INTRODUCTION

As a high temperature wide bandgap semiconductor (3.23 eV) with high index of refraction (2.7), high fracture toughness (3.1 MPa-m0.5), high thermal conductivity (~5.0 W/cm), high saturated electron drift velocity (~2.7 x 10^7 cm/s) and high breakdown electric field strength (~3 MV/cm), SiC is a material of choice for high temperature, high voltage, high frequency and high power applications. The large S-C bonding energy makes SiC resistant to chemical attack and radiation which makes it a suitable candidate as a material for multi-functional purposes, e.g. for device fabrication in harsh environments [1-3].

Recently, it has been shown that SiC can be employed as both an oxygen and a hydrogen sensor that operates in a temperature regime considerably higher than conventional sensors such as tin oxide (SnO2) or silicon. Because of its outstanding thermal stability, silicon carbide can be employed as a hydrogen and hydrocarbon sensor that can potentially operate at temperatures up to 1000°C [4-9]. Potential uses of elevated temperature SiC sensors include automotive applications, process gas monitoring, aeronautics, remote optical sensors, and aerospace applications.

A: SiC GAS SENSOR

The deposition of a catalytic metal such as Palladium (Pd) onto silicon carbide (SiC) results in Schottky diode behavior. The adsorbing gas changes the space charge region under the metal clusters which in turn affect the conductivity of the crystal. This change in conductivity is measured and can be correlated to surface concentrations and to the levels of the sampled gas in the ambient. The high sensitivity for hydrogen containing combustible gases is enhanced by the presence of catalytic metals. Hydrogen containing species dissociatively adsorb to the metal and hydrogen atoms migrate to the Pd/SiC interface where they affect the current-voltage (I-V) properties of the SiC [8]. Rather than applying a palladium film [9], we have implanted palladium ions into the silicon face of 6H, n-type SiC samples.

The implantation was performed at 500°C, in order to minimize the induced implantation damage, to fluences between 3x10^14 at/cm² and 3.2x10^16 at/cm², and implantation energies of 70 keV and 130 keV. The implantation energies were chosen using the SRIM code [10] in order to get high near surface concentrations of Pd ions. Also, from the same code, the approximate implantation range was established as being 40 nm and 65 nm (see figure 6).

The current measurements were done for temperatures near 23, 70, 145, 215°C in a closed gas environment. Voltages of ±1V were applied on the backside of the sample, and the current was measured using a probe on several places on the implanted side. The temperature was also monitored in order to correct for current fluctuations due to temperature changes. For this experiment, air was cycled with an H₂-Ar gas mixture with 4% hydrogen, and the cycles were chosen to be 2 minutes in length (a compromise between the signal rise time and the length for a complete measurement of 7 cycles). A drawing of the experimental setup is shown in Fig. 1. The metallic contacts were made of...
gilded copper, and the insulator was thick Teflon, so that the capacitance with the bottom side of the aluminum enclosure (connected to the common ground as a Faraday cage) was negligible.

![Diagram](image)

**Figure 1.** Schematic view of the setup.

**RESULTS**

Figures 2 through 5 show that at room temperature (23°C) the current increases in the presence of the 4% H₂ in the H₂-Ar mixture, for all of the SiC implanted samples.

![Graphs](image)

**Figure 2.** Current response for 6H SiC sample implanted with $3 \times 10^{14}/cm^2$, 130 keV Pd; positive voltage applied.
Figure 3. Current response for the same sample as in Fig. 2, negative voltage applied.

Figure 4. Current response for a sample implanted with $3.2 \times 10^{16}/\text{cm}^2$, 130 keV Pd; positive voltage applied.
When the H₂–Ar environment is replaced by air, the current reverts to its initial value. At higher substrate temperatures, the differential current for H₂–Ar ambient and air ambient decreases as the substrate temperature approaches 60°C to 84°C and then it is reduced to zero. As the temperature increases, as shown in these figures, the substrate current in the presence of H₂–Ar gas is smaller than when air is present. Measurements were, also, performed on pristine SiC samples which revealed no current differential with the gas change for temperatures from 23°C to 240°C. The current measurement of the sensors produced at high implantation temperatures shows behavior while exposed to hydrogen, opposite to that for sensors reported in the literature [4, 6, 9] for SiC with palladium deposited on the surface. There, the measured current in the presence of hydrogen is more for every temperature level, and reverts to the initial value when air is supplied instead of hydrogen.

A similar behavior was observed for both positive and negative voltages applied (the currents for negative voltage are shown in the Figures 3 and 5 in absolute values). For absolute voltages above 1.2 V, the p-n junction breaks down, and no more sensing behavior can be observed.

The current measurement for sensors produced at low implantation fluence is smaller than the current measured for sensors produced at high implantation fluence, at the same implantation energy. The sensors produced at lower implantation energies showed higher current sensitivity than the sensors produced at higher implantation energies (deeper implanted layer, Figure 6). Also, the fact that after the p-n junction breakdown no more sensing behavior can be observed makes us believe that the sensing properties are related to the rectifying properties of the device rather than strictly due to the modification in the conductivity of palladium, or palladium hydride. If we accept this observation, then the similar behavior for both positive and negative voltages applied might be due to a structure more like n-p-n rather than simple p-n junction. This is expected, since the crystallinity of the SiC layer remains unchanged during high temperature implantation.

The relatively long rise time that can be observed on all the graphs presented in figures 2 to 5 is due to the fact that the hydrogen has to diffuse through the surface layer to reach the deeper palladium ions as the ones close to the surface become saturated. Similarly, when air is introduced, the diffusion process is reversed, from the depth to the surface, resulting in the long recovery time. The recovery process is based on the capability of removal of the hydrogen that was adsorbed in the device. Two processes occur: the chemical affinity for hydrogen by the oxygen in the air, and the outgassing due to the device’s operation at elevated temperatures. At room temperature the first process is dominant, while the outgassing begins to contribute at temperatures above 100°C.
B: NANO-CLUSTERS IN SiC

It has been shown that introducing metal colloids such as gold into an optical material, such as glass matrix, will change the color of the material. These materials have long been used for decoration and more recently have been used to fabricate optical devices. In recent years, more attention has been given to both linear and nonlinear properties of the material caused by optical absorption due to the surface plasmon resonance frequency, which depends on the index of refraction of the host substrate and the electronic properties of the colloids formed in the host material. The nonlinear properties allow the manufacturing of a wide range of optical devices. Ion implantation followed by thermal annealing has been used to introduce similar effects near the surface as well as to change the nonlinear optical properties [10-14]. An attractive property of ion implantation is that the ions can be focused to introduce the linear and nonlinear properties in a well defined space in an optical device.

We present the results of our investigation of producing nanoclusters of gold, silver, copper and tin in 6H and 4H-SiC. In this work we study the changes in the linear optical properties as a function of ion fluence and post-implantation heat treatment. We implanted 1.0 MeV Au, 2 MeV Ag and Cu and 120 and 160 keV Sn into the Si face of SiC at 30 or 500°C followed by annealing at various temperatures.

It has long been known that small metallic particles or colloids embedded in dielectrics produce colors associated with optical absorption at the surface plasmon resonance frequency [15, 16]. For clusters with diameters much smaller than the wavelength of light (λ), the theories of Mie [17] can be used to calculate the absorption coefficient of the composite:

\[
a = \frac{18\varepsilon_0 n_0^3}{\varepsilon_1} \frac{\mu_0}{(\varepsilon_1 + 2n_0^2)^2 + \varepsilon_2^2}
\]

where \(Q\) is the volume fraction occupied by the metallic particles, \(n_0\) is the refractive index of the host medium, and \(\varepsilon_1\) and \(\varepsilon_2\) are the real and imaginary parts of the frequency-dependent dielectric constant of the bulk metal. Equation 1 is a Lorentzian function with a maximum value when the light frequency equals the surface plasmon resonance frequency \(\omega = \omega_p\), where
Values of $\varepsilon_i$ for the metals as a function of wavelength are tabulated in [18] and the published index of refraction for SiC is 2.655. The index of refraction measured by prism coupling for the SiC used in this work was 2.26. From Equation (2) one can predict the photon wavelengths for the surface plasmon resonance frequencies for metallic colloids in the photorefractive host materials, as shown in figure 7 ($\varepsilon_i$ vs. Wavelength). This figure shows that taking $n_0 = 2.7$, the theoretical value of $n_0$ for SiC, the absorption bands should be near 691 nm, 578 nm, 668 nm, and 446 nm for Au, Ag, Cu, and Sn colloids, respectively. Similarly for the in-house measured index, $n_0 = 2.26$, the absorption bands for SiC with Au, Ag, Cu, and Sn colloids shift to 625 nm, 599 nm, 617 nm, and 382 nm, respectively.

We have implanted SiC samples from CREE Research Inc., (6H-N type, 3.5° off axis, doped with nitrogen at 9.2 x 10^{17}/cm³, Si face) with ions such as 1.5 MeV Si, 1.0 MeV Au, 2.0 MeV Ag, 2.0 MeV Cu, and 160 keV Sn at fluences between $8 \times 10^{15}$/cm² to $5 \times 10^{17}$/cm² both at room temperature and at 500°C. In our previous work on various other optical materials, we used either an energetic inert ion such as He or Ar or an ion which is one of the constituents of the host crystal, such as Si or O, to observe the change in the optical properties of the bombarded material as a function of the implantation parameters. Figure 8 shows the optical absorption spectra for SiC bombarded by 1.5 MeV Si ions at various fluences, at room temperature and at 500°C. The room temperature bombardment caused severe darkening, even at fluences as low as $4 \times 10^{16}$/cm², red-shifting the absorption edge from 350 nm to 650 nm and causing an overall increase in the absorption baseline. Implantation at elevated temperature, 500°C, displayed a textbook behavior. That is, red-shifting the absorption edge at higher fluences, while allowing the damage to recover, even at such low temperature. The reason we selected Si as a test ion is because Si is one of the constituents of the SiC crystal and the absorption band for Si nanocrystals is in the far IR region and will not interfere with our measurements. These spectra from the Si bombardment were then used as baselines to subtract the optical absorption due to ion bombardment damage.

Figure 9 shows optical absorption spectrum for a 6H, N doped SiC sample implanted with $3 \times 10^{17}$ Au/cm² at 1.0 MeV and at a temperature of 500°C then annealed at 1000°C in an argon ambient for one hour. Also shown is the absorption spectrum of the sample prior to implantation and the difference between the two. At Au fluences less than $3 \times 10^{17}$ cm²/cm²
no peaks due to plasmon resonance were discernible. It is clear from the difference spectrum that significant implantation damage remains after the heat treatment. Similar effects were observed in 6H, N-doped SiC, as shown in Fig. 10. The peak was at 535 nm after heat treatment at 1100°C in air. The peak was expected to appear in the range of 630 to 680 nm, depending upon the value of the refractive index after implantation. Using Eq. 2 and Fig. 7 the index would need to change from 2.7 to 1.5 to account for the location of the plasmon resonance peak. One possible explanation is that SiO₂ is formed during the annealing process. If this is so it indicates that the Ar atmosphere used in annealing the sample is Fig. 9 failed to purge the O completely. Rutherford backscattering analysis has indicated the presence of oxygen in the both implanted and unimplanted areas of the sample, but the oxide layer was 20 percent thicker (170 nm vs. 140 nm) on the implanted side than on the unimplanted side. Approximately 10 to 20 percent of the gold atoms were in the oxide layer.

The size of the Au clusters can be estimated from the peak position and the width of the resonance through the relation \( r = \frac{\Delta m v_f}{\Delta \omega} \) [1] where \( \Delta m \) is a constant, taken to be 1.5 for Au, \( v_f \) is the Fermi velocity of electrons in gold and \( \Delta \omega \) is the full width at half maximum of the absorption peak. From Fig. 9 the Au cluster diameter is estimated at 5 nm. The cluster diameters in Fig. 10 are estimated to be at least 4 nm for the \( 5 \times 10^{17} \) ion/cm² implant and 6 nm for the \( 3 \times 10^{17} \) ion/cm² implant.

![Figure 9. Optical Density vs. Wavelength for 1 MeV Au implanted at room temperature into 6H, N-doped SiC. Ion fluence was \( 3 \times 10^{17} \) ion/cm². Sample was heated in Ar to 1100°C.](image)

![Figure 10. Optical Density vs. Wavelength for 1 MeV Au implanted at 500°C into 4H, Al-doped SiC then heated in air to 1100°C for 1 hr. Bottom trace is optical absorption of the unimplanted sample.](image)

Figure 11 shows the absorption band obtained from a SiC crystal bombarded by 2.0 MeV Ag at 500°C at \( 1.1 \times 10^{17} \) ion/cm² and annealed at 1000°C in argon for one hour. The optical absorption spectra shown has had the baseline subtracted. Using the centroid of the peak, 493 nm, and equation (2), the calculated index of refraction for SiC at the implanted volume is 2.15. It is important to subtract the absorption due to bombardment damage using a bombarded SiC as a reference sample in the experiment. In figures 11 and 12, for Ag and Cu implanted at 500°C, the baseline is a sample implanted with the same ion at room temperature. A negative value can result at wavelengths where the increase in the optical density induced by the ion beam damage for room temperature implantation is greater than that created by elevated temperature implantation.

Figure 12 shows the absorption band obtained from a SiC crystal bombarded by 2.0 MeV Cu at 500°C, at \( 3 \times 10^{17} \) ion/cm² and annealed at 900°C, in argon for ninety minutes. The optical absorption band for Cu implanted SiC is weak and falls at the same vicinity as the natural optical absorption of the nitrogen doped SiC, 630 nm. Using the centroid of the peak, 659 nm, and equation (2), the calculated index of refraction for SiC at the implanted volume is 2.65, which is...
the same as the theoretical value [12]. The measured location of the absorption band for Cu implanted SiC is at the upper limits of where it should be and the calculated index of refraction for the SiC in the implanted volume is higher than that observed for the virgin crystal. Since the measured absorption band is red shifted, this anomaly cannot be attributed to the natural absorption band of the nitrogen-doped SiC.

Figure 13 shows typical optical absorption spectra for SiC implanted with 160 keV Sn at room temperature and annealed at 200°C in argon for one hour. This figure also shows that as implantation fluence increases the absorption baseline increases. Using the measured absorption band, 406 nm, and equation (2) the calculated index of refraction for SiC at the implanted volume is 2.22. Increasing the Sn fluence produced an increase in the height of the optical absorption band due to formation of Sn nanoclusters. Observation of the formation of Sn nanoclusters in SiC using visible optical spectrometry was made possible because of the high index of refraction of the host material. Otherwise, the absorption band would have been located in the UV region.
Implantation at room temperature results in a large increase in optical absorption that can mask the surface plasmon resonance absorption band. This difficulty is alleviated by implanting at elevated temperature (500°C), which inhibits the formation of defects. The broad plasmon resonance spectra indicate that the nanoclusters are very small. Further work is necessary at higher implantation and annealing temperatures.

CONCLUSIONS

In this manuscript we discussed only two of the applications of the SiC crystals: 1) application for fabrication of electronic sensors; 2) application for fabrication of optical devices. Because of its hardness, SiC is typically used for surface coating and recently for fabrication of windows and mirrors used in the harsh environment of space.

The latter application, fabrication of optical devices, is rather new. The high index of refraction in SiC, 2.655, gave us the edge to observe the absorption spectra due to Sn nanoclusters. The strength of Si-C band as well as the diffusivity of metals in SiC should be used to study the possibility of formation of epi-layer of nanoclusters for various materials with high volume fraction, which will enable us to use much lower implantation dose and use lower power lasers to operate optical devices.

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