The need to sense chemical mixtures in a variety of hostile environments (such as high temperature caustic gases) continues to grow. However, silicon electrical devices are limited to relatively low temperatures \(< 250 \text{ °C}\). For this reason, wide bandgap materials such as silicon carbide have received increased attention. Current SiC sensors such as Schottky diodes composed of catalytic metals show deficiencies such as unacceptable drift in the signal. Alternative sensor structures, such as porous semiconductors, may provide improved sensor performance.

A novel electroless method of producing porous silicon carbide (PSiC) is presented. Unlike anodic methods of producing PSiC, the electroless process does not require electrical contact during etching. Rather, platinum metal deposited on the wafer before etching serves as a catalyst for the reduction of a chemical oxidant, which combined with UV illumination injects holes into the valence band, the holes subsequently participating in the oxidation and dissolution of the substrate. The etchant is composed of HF and \( \text{K}_2\text{S}_2\text{O}_8 \) in water. Various porous morphologies are presented as a function of etchant concentration, time of etching, and SiC polytype. High surface areas of \(~150 \text{ m}^2/\text{cm}^2\) are attainable. Wafer quality is found to be of the utmost concern when utilizing the electroless wet etchant, since defects such as stacking faults, dislocations, and micropipes have a large impact on the resulting porous structure.

Results of imaging and spectroscopic characterization are presented and compared to PSiC produced via anodic etching of the same wafer material. In general, it is found that electrolessly etched PSiC has photoluminescent, cathodoluminescent, and Raman scattering properties relatively unchanged from bulk SiC. However, the spectroscopic properties of the anodically etched PSiC were dramatically different than those found for bulk SiC. Cathodoluminescence studies of anodically etched porous layers yield luminescence peaks in the ultraviolet region (energies higher than the bandgap energy of bulk SiC). Fig. 1 shows cathodoluminescence spectra of unetched 6H-SiC and three different pieces of PSiC prepared from n-type 6H-SiC by anodic etching for 40 min. The three PSiC samples all show peak UV emission blue of the bandgap emission at 426 nm. The variability of the peak cathodoluminescence wavelength could be an indication of quantum confinement effects. Additional spectroscopic results (photoluminescence, Raman emission) have been collected from the same porous films in order to determine the origin of the UV cathodoluminescence emission. The photoluminescence from these samples showed a wide variability of peak position; thicker porous layers generally lead to the greater photoluminescent blueshifts. However, no UV photoluminescence was witnessed. Raman scattering spectra show the development of Fröhlich modes as the thickness of the porous layer increases. Therefore, although quantum confinement is one possible cause of the UV cathodoluminescence, other spectroscopic results indicate that defect structures or surface state species are the most likely origin of the UV emission.
Anodically etched PSiC films are then investigated for their suitability as chemical and temperature detectors particularly suited for high temperature, caustic environments. Studies utilizing interferometry\textsuperscript{7,8} as well as conductivity\textsuperscript{9,10,11} have been conducted. PSiC layers were unresponsive in interferometry for a wide variety of adsorbate gases, and this method of analyte detection proved unsuccessful.

![Figure 1](image_url)

Ohmic contacts\textsuperscript{12,13} to PSiC were fabricated in order to study changes in the bulk conductivity of the porous semiconducting skeleton when exposed to various chemical and temperature conditions. Conductometric investigations show that PSiC has a measurable response to high concentrations of hydrogen gas (~6\% decrease in resistance when exposed to 20\% H\textsubscript{2}) comparable to platinum alloy resistive films currently used in hydrogen sensing arrays.\textsuperscript{14} However, similar to the resistive films, strict temperature control of the PSiC sensor is necessary. As a result, current hydrogen sensing arrays may be improved by the introduction of a PSiC sensor for the specific role of high concentration sensing. Eventually, it may be possible to form an array of PSiC sensors capable of distinguishing the concentrations of individual components within a gas flow as well as the temperature of the gas flow.

References


