

Date: June 20, 2002

To: NASA Grant Administrator

From: Prof. Leonard J. Brillson

Subject: Glennan Microsystems Initiative Final Report for Project 755-9E-00-00-400-2-0-29-4111-2 YOJ1297 under Grant/Cooperative Agreement NCC3-949

During the 2001-2002 award period, we performed research on Pt/Ti/ bare 6H-SiC and bare 4H-SiC interfaces in order to identify their electronic properties as a function of surface preparation. The overall aim of this work is to optimize the electronic properties of metal contacts to SiC as well as the active SiC material itself as a function of surface preparation and subsequent processing. Initially, this work has involved identifying bare surface, subsurface, and metal-induced gap states at the metal-SiC contact and correlating energies and densities of deep levels with Schottky barrier heights. We used low energy electron-excited nanoluminescence (LEEN) spectroscopy, X-ray photoemission spectroscopy (XPS), and Secondary Ion Mass Spectrometry (SIMS) in order to correlate electronic states and energy bands with chemical composition, bonding, and crystal structure. A major development has been the discovery of polytype transformations that occur in 4H-SiC under standard microelectronic process conditions used to fabricate SiC devices. Our results are consistent with the stacking fault generation, defect formation, and consequent degradation of SiC recently reported for state-of-the-art ABB commercial diodes under localized electrical stress. Our results highlight the importance of optimizing process conditions and material properties - anneal times, temperatures and doping to control such structural changes within epitaxial SiC layers. Thus far, we have established threshold times and temperatures beyond which 4H-SiC exhibits 3C-SiC transformation bands for a subset of dopant concentrations and process conditions. On the basis of this temperature-time behavior, we have been able to establish an activation energy of  $\sim 2.5$  eV for polytype transformation and dislocation motion. Work continues to establish the fundamental mechanisms underlying the polytype changes and its dependence on material parameters.

LEEN measurements taken over a range of incident electron beam energies provide a means to identify the presence of localized states and their spatial distribution on a nanometer scale. With increasing incident electron beam energies  $E_B$ , the electron cascade and resultant generation of free electron-hole pairs occur at increasing depths, ranging from 15 nm at 1 keV to 180 nm at 4 keV for the nucleon values and material densities involved here. Excitation rates peak at one-third of these depths. These electron-hole pairs excite band-to-band and band-to-defect transitions that we detect optically, even through the thin metal contact layer of the metal-SiC junction. Thus it is possible to excite luminescence selectively, either at the intimate metal-SiC

interface, the near-interface region extending tens of nanometers into the SiC, or the bulk SiC up to 0.2 microns within the solid.

Ohio State University graduate students Sergey Tumakha with assistance from Gregg Jessen performed LEEN spectroscopy on a set of Pt/Ti/SiC junctions provided by Dr. Robert Okojie at NASA Glenn. They used a high efficiency monochromator, charge coupled device (CCD) detector, and fiber optic cable photon collector developed with previous NASA support. Using this equipment in an Ohio State ultrahigh vacuum (UHV) chamber, they were able to acquire sets of depth-dependent LEEN spectra for over 70 specimens. This wide array of samples permitted us to identify systematic dependences on initial polytype, temperature, anneal time, process step, and doping.

We used LEEN spectroscopy and XPS to probe deep level defect states at interfaces of 4H and 6H-SiC with Ti/Pt metallization. These studies aim to identify process conditions under which thermally-stable ohmic and Schottky contacts can be obtained on SiC while minimizing the formation of deep level electronic states. Depth-dependent LEEN measurements establish the presence of localized states and their spatial distribution on a nanometer scale. Spectra from the near interface region of 6H-SiC indicate the existence of a SiC polytype with a higher band gap of  $\sim 3.4$  eV. Excitation of the intimate metal-SiC interface reveals a process-dependent discrete state deep within the SiC band gap. XPS measurements reveal consistent differences in the C 1s chemical bonding changes with specific process steps. Analogous chemical treatments of 4H-SiC also produce a lower band gap SiC polytype with  $\sim 2.5$  eV energy extending tens of nanometers beyond the interface – confirmed by transmission electron microscopy (TEM). This work is the first to show the effect of metal-semiconductor interactions not only on localized states but also on the lattice structure of the semiconductor near the interface.

Figure 1(a) illustrates the depth-dependent optical emission spectra from 6H-SiC after an acetone/methanol clean, a 4-hour oxidation at 1150 °C, followed by a deionized (DI) water rinse and Pt/Ti metallization. In addition to the expected emission at 2.9 eV corresponding to bulk 6H-SiC, this panel shows an additional shoulder at 3.3 eV corresponding to a new polytype for excitation energies near the SiC-metal interface. Such changes are consistent with NASA-Glenn transmission electron microscopy (TEM) images in cross section that show altered atomic layer stacking over the transition region extending less than 50 nm between the SiC and the metal. A broad continuum of states is also evident at near-interface excitation energies. A subsequent Pirhana etch produces the depth-dependent features shown in Fig. 1(b). In addition to the features evident in fig. 1(a), the Pirhana etch induces new emission at 1.9 eV at the intimate 6H-SiC interface. Such emission corresponds to a near-mid-gap localized state. Comparison of figs. 1 (a) and (b) illustrates that surface treatments prior to metallization can induce pronounced electronic changes at the metal-6H-SiC interface.

Figure 2(a) illustrates the depth-dependent optical emission spectra from 4H-SiC cleaned with acetone/methanol, then metallized with Pt/Ti. In addition to the expected emission at 3.2 eV corresponding to bulk 4H-SiC, this panel shows an additional shoulder just above 3.2 eV, corresponding to a new polytype for excitation energies near the SiC-metal interface. As with the 6H result in fig. 1, a broad continuum of states is also evident at near-interface excitation energies corresponding to disorder-induced interface states. The analogous interface involving 4H-SiC cleaned with acetone/methanol, then oxidized at 1150 °C, DI rinsed, then finally metallized with Pt/Ti appears in fig. 2(b). This panel illustrates a dramatic change with oxidation, namely, the appearance of a pronounced new emission peak at 2.5 eV. This emission

dominates the weak 4H-SiC bulk emission for all excitation depths extending beyond 50 nm. It indicates the formation of a new polytype with a smaller band gap. We believe this emission is due to formation of 3C-SiC with quantum scale dimension in a direction perpendicular to the basal plane. Such a transformation is evident from high resolution TEM images taken in cross section for this sample by Ming Zhang and Pirouz Pirouz at Case Western Reserve University.

We then focused on the nature of the 4H-SiC polytype transformation. Figure 3 illustrates temperature-dependent LEEN spectra for a 4H-SiC sample cleaned with acetone/methanol, oxidized at different temperatures, DI rinsed, then finally metallized with Pt/Ti. The spectra show the bulk 4H-SiC clearly for all the low temperature spectra. At 1000°C, the 2.5 eV peak indicative of the transformation appears after a 2.5 hour anneal. There are no further increases in this peak relative to the bulk 4H-SiC at higher temperatures, indicating that 1000°C is a threshold for polytype transformation. Interestingly, above 1200°C, this feature actually decreases as other excitations become more pronounced, including the bulk 4H-SiC peak at 3.2 eV. This result shows that the 3C-SiC formation is limited in nature, diminishing with additional processing.

Figure 4 illustrates time-dependent LEEN spectra for a 4H-SiC specimen cleaned with acetone/methanol, oxidized at 1150°C for different times, then DI rinsed, and Pt/Ti metallized. As shown, the bulk 4H-SiC peak decreases with increasing anneal time while the 2.5 eV 3C-SiC feature grows. This figure shows that the 3C-SiC feature begins to emerge after 1 hour and becomes dominant after 1.5 hours. No further changes are evident at longer oxidation times. This result implies that the 3C-SiC formation is limited. No further increase occurs after extended annealing times, consistent with a strain release mechanism.

Perhaps most dramatic of all, Figure 5 demonstrates that the transformation process occurs even with oxidation. The figure shows LEEN spectra for a 4H-SiC sample after acetone/methanol clean, after subsequent Pirhana clean, and finally after 1150°C anneal in argon. Clearly the surface cleaning methods do not appear to induce the transformation. Only after argon annealing does this feature appear. These results demonstrate that 4H-SiC can transform the 3C-SiC with annealing alone, i.e., without an oxidation process.

Finally, Figure 6 shows the optical emission spectra after acetone/methanol cleaning, oxidation at 1150°C, DI rinse, and Pt/Ti metallization for 4H-SiC specimens as a function of epilayer bulk doping. The  $n=1.7 \times 10^{19} \text{ cm}^{-3}$  spectrum displays the 2.5 eV 3C-SiC feature, similar to the spectra in fig. 2(b). The other spectra show that high doping produces new features at 2.0, 2.2, and 2.7 eV. The 2.5 eV feature is in fact dominant only for the  $n=1.7 \times 10^{19} \text{ cm}^{-3}$  doping concentration. Besides the bulk 3.2 eV 4H-SiC peak and the 2.5 eV feature, the other features correspond to defects within the volume probed. The strong dependence on doping indicates that dopants play a role in changing the strain within the semiconductor. This is consistent with X-ray diffraction measurements of Dr. Robert Okojie showing increasing strain with doping due to the atomic size difference between N and C in the SiC lattice.

More detailed descriptions of the experimental results are to be found in interim reports already submitted to Dr. Okojie throughout FY 2001. Additional results can be provided upon request.

### **Journal Articles Published or Submitted**

1. R.S. Okojie, D. Lukco, M. Xhang P. Pirouz, S. Tumakha, G. Jessen, and L. J. Brillson, "Direct Observation of Oxidation-Induced 4H-SiC – 3C-SiC Polytypic Transformation," *Appl. Phys. Lett.*, in press (2001).
2. S. Tumakha, L.J. Brillson, G.H. Jessen, R.S. Okojie, D. Lukco, M. Zhang, and P. Pirouz, "Chemically-Dependent Traps and Polytypes at Pt/Ti Contacts to 4H and 6H-SiC," *J. Vac. Sci. Technol.*, B 20, 554 (2002).
3. "4H- to 3C-SiC Polytypic Transformation During Oxidation," R.S. Okojie, M. Xhang, P. Pirouz, S. Tumakha, G. Jessen, and L.J. Brillson, *Mater. Sci. Forum Vols. 389-393* (2002), pp. 451-454. (Trans Tech. Pub. Ltd, Zurich, 2002).
4. "Surface Morphology and Chemistry of 4H- and 6H-SiC After Cyclic Oxidation," R.S. Okojie, D. Lukco, L. Keys, S. Tumakha, and L. J. Brillson, *Mater. Sci. Forum Vols. 389-393* (2002), pp. 1101-1103. (Trans Tech. Pub. Ltd, Zurich, 2002).
5. "Thermal and Doping Dependence of 4H-SiC Polytype Transformation," L.J. Brillson, S. Tumakha, G.H. Jessen, R.S. Okojie, M. Zhang, and P. Pirouz, *Appl. Phys. Lett.*, submitted (2002).

### **Conference Papers Presented**

1. "Chemically-Dependent Traps and Polytypes at Pt/Ti Contact to 4H and 6H-SiC," S. P. Tumakha, L. J. Brillson, G.H. Jessen, R.S. Okojie, D. Lukco, *Electronic Materials Conference, South Bend, IN, June 29, 2001.*
2. "Defects and Interface Chemistry at III-V Nitride and SiC Surfaces and Interfaces," *Workshop on Near-surface Effects in Semiconductor Substrates, Kodiak Island, Alaska, August 5, 2001 (Invited)*
3. "Metal-Induced States and Polytype Transformations at SiC Interfaces," S. Tumakha, L.J. Brillson, G.H. Jessen, R.S. Okojie, D. Lukco, *IUVSTA 15<sup>th</sup> International Vacuum Congress, AVS 48<sup>th</sup> International Symposium, 11<sup>th</sup> International Conference on Solid Surfaces, San Francisco, CA, October 29, 2001.*
4. "Doping and Temperature Effects on Strain in N-Type 4H-SiC Epilayers," r.S. Okojie, M. Zhang, P. Pirouz, L.J. Brillson, S. Tumakha, and G. Jessen, *Electronic Materials Conference, Santa Barbara, CA, June 28, 2002.*

### **Awards**

1. Ohio State University Lumley Research Award (2001)
2. Office of Naval Research Outstanding Speaker Award (2001)
3. Fellow, American Association for the Advancement of Science (2002)

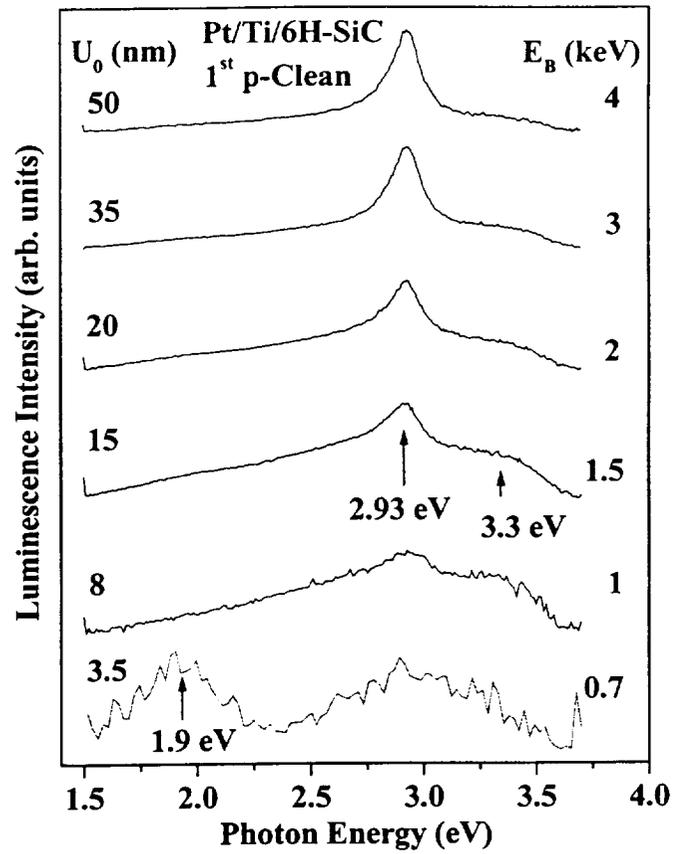
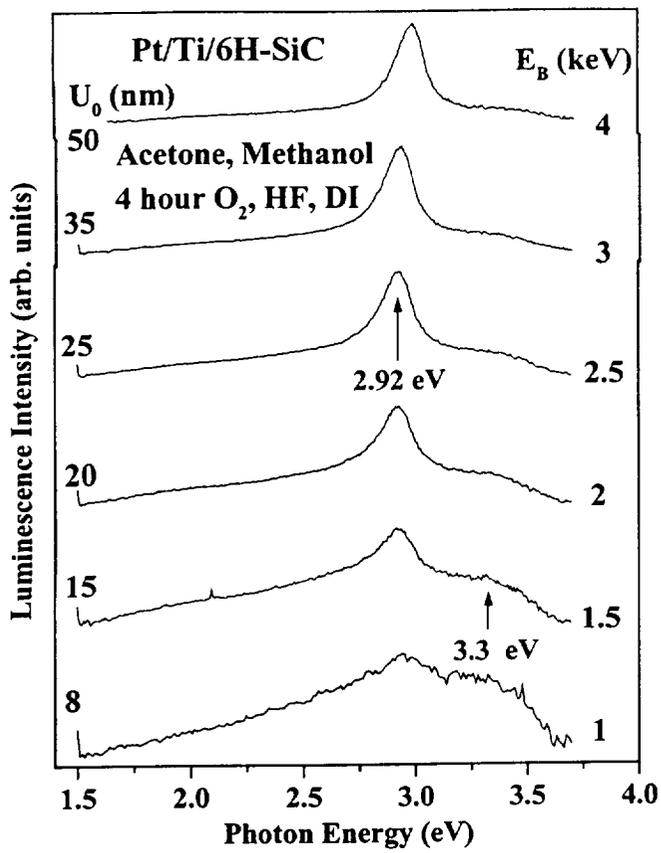


Figure 1. Depth-resolved 6H-SiC LEEN spectra before and after P-cleaning.

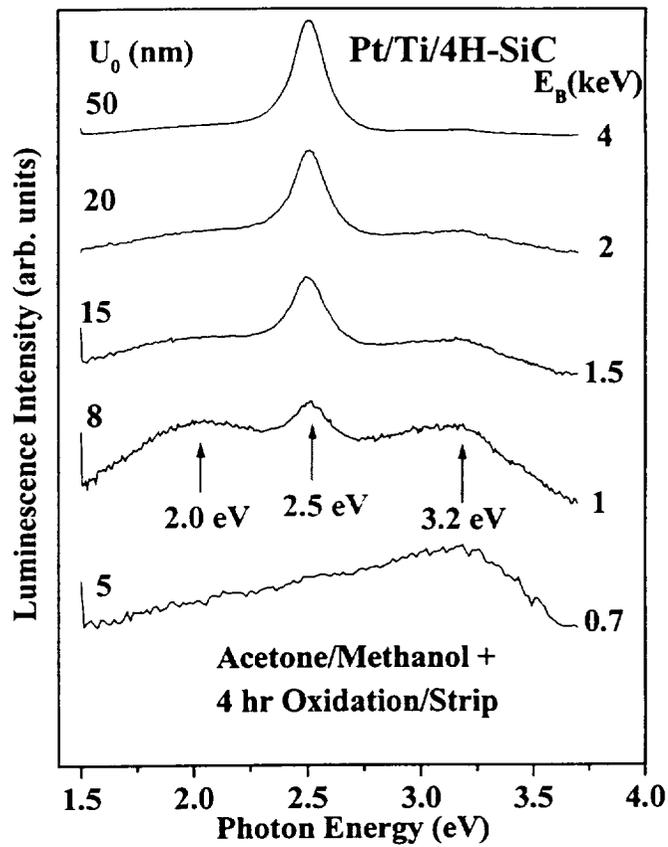
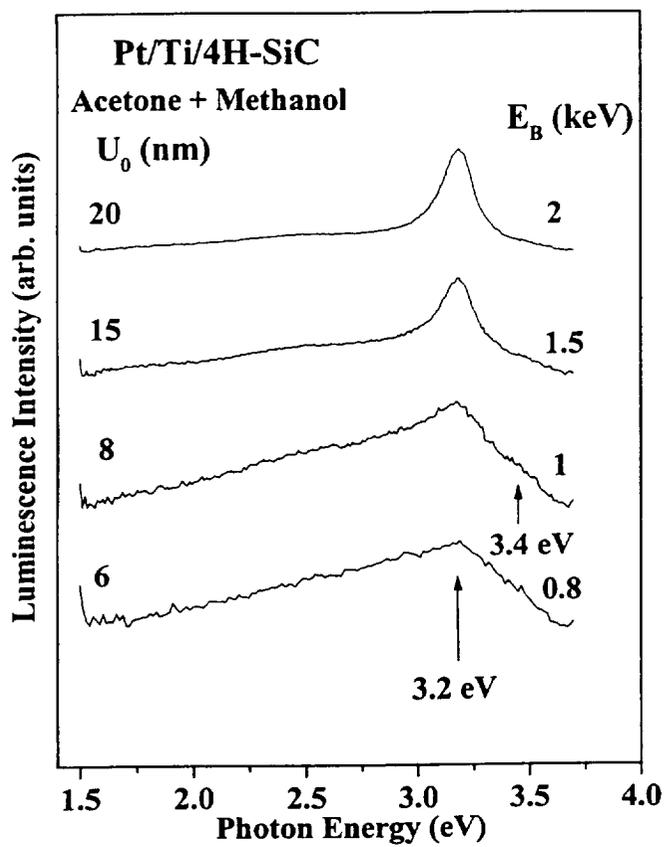


Figure 2. Depth-resolved 4H-SiC LEEN spectra before and after oxidation.

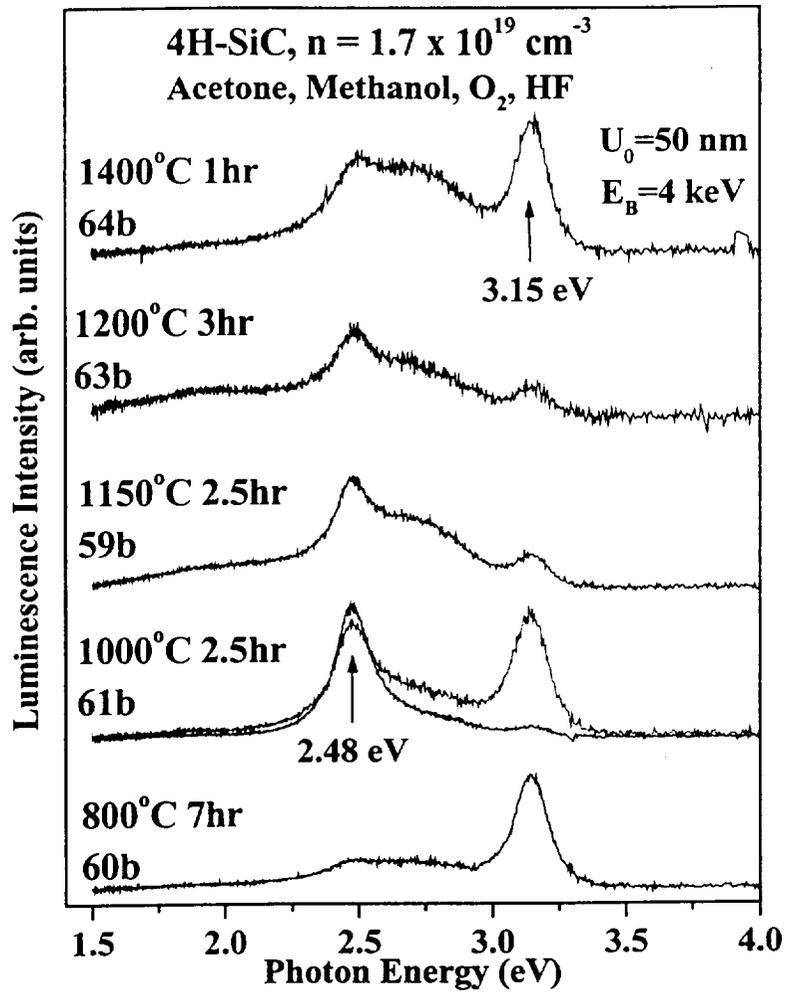


Figure 3. Depth-dependent LEEN spectra of 4H-SiC as a function of oxidation temperature.

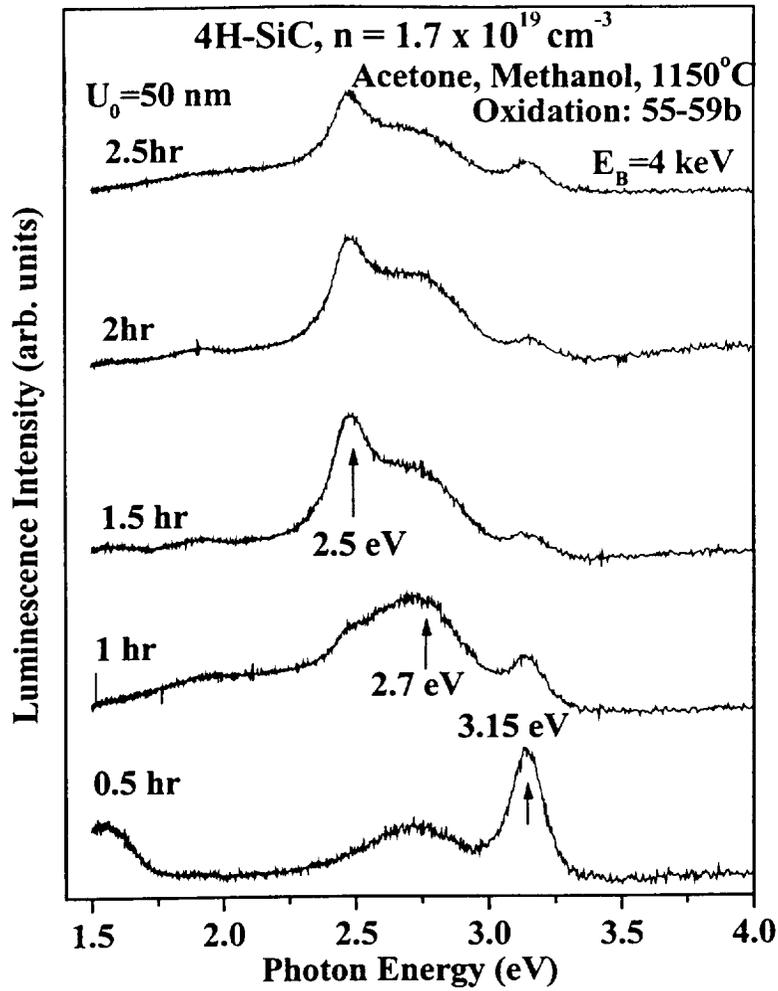


Figure 4. Depth-resolved 4H-SiC LEEN spectra as a function of oxidation time at  $1150^\circ\text{C}$ .

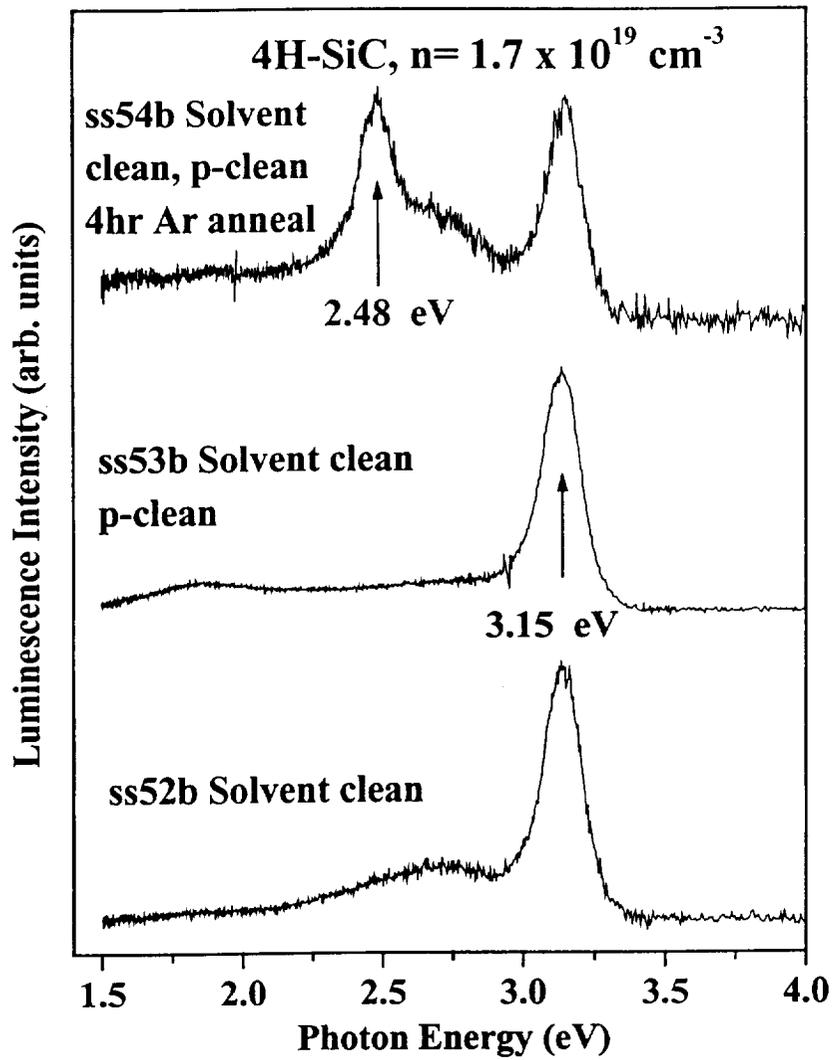


Figure 5. 4H-SiC LEEN spectra as a function of surface cleaning and annealing.

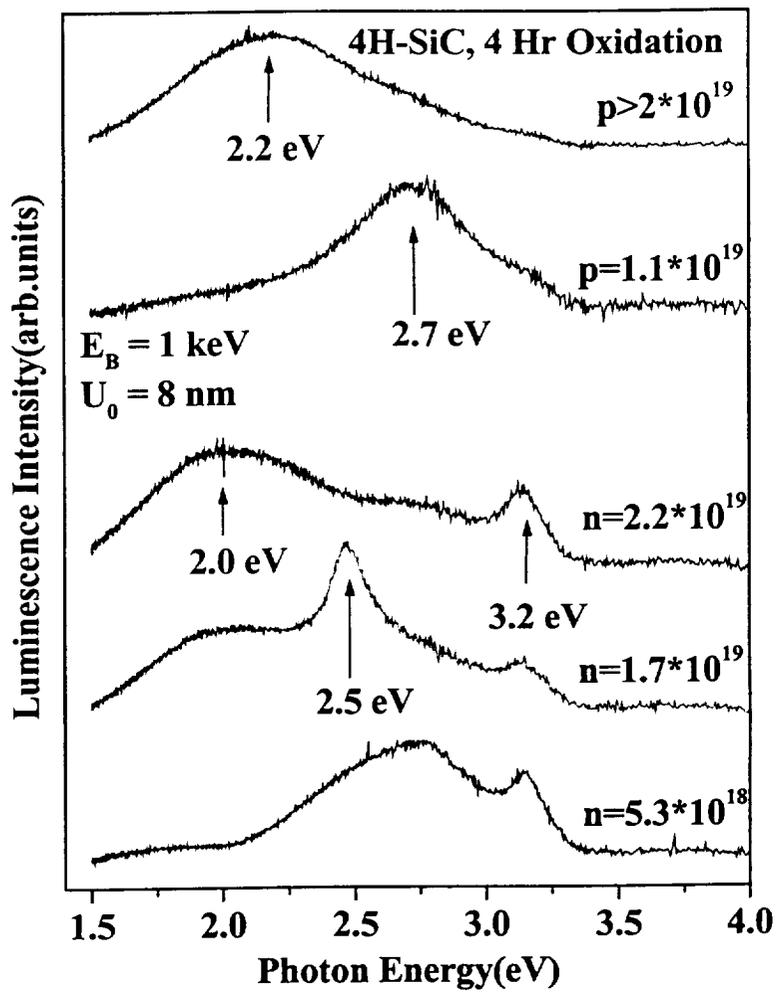


Figure 6. 4H-SiC LEEN spectra as a function of doping.