Characterization of Buffer Layers for Remote Plasma-Enhanced Chemical Vapor Deposition of Germanium-Tin Epitaxial Layers

S. Zollner,[1] C. A. Armenta,[1] B. Rogers,[2] G. J. Grzybowski,[3,4] B. Claflin[4]
[1]*Dept. of Physics, New Mexico State University, Las Cruces, NM, USA*
[2]*Dept. of Chemical and Biomolecular Eng., Vanderbilt University, Nashville, TN, USA*
[3]*KBR, 3275 Pentagon Boulevard, Beavercreek, OH 45431, USA*
[4]*Air Force Research Laboratory, Sensors Directorate, WPAFB, OH 45433, USA*

Germanium-tin alloys are of interest for infrared light detectors to increase capabilities in image and data capture and transmission, because they can have a direct band gap with more than about 7% tin. Remote plasma-enhanced chemical vapor deposition (RPECVD) is attractive for growth of Ge-Sn alloys because it enables low-temperature epitaxy on Si using common precursors GeH_4 and $SnCl_4$. The growth of such epilayers can be optimized with an initial high-temperature buffer layer. This work focuses on the characterization of this buffer layer using atomic force microscopy, ellipsometry, thin-film powder x-ray diffraction, and x-ray photoelectron spectroscopy (XPS) for different growth conditions.

Thin Ge and Ge-Sn buffer layers with 10-20 nm thickness were deposited on Si (100) substrates for one minute at temperatures from 360°C to 500°C with varying SnCl4 precursor flows mixed with GeH4 and helium. Ellipsometry spectra for all films show critical point structures in the E_1, $E_1+\Delta_1$, and E_2 region of Ge, indicating that all layers are crystalline. A layer grown at 360°C without $SnCl_4$ can be described reasonably well as an 11 nm thick layer of crystalline germanium with 2 nm of roughness. Adding $SnCl_4$ to the gas flow significantly reduces the height of the ε_2 maximum at E_2, indicating that the layer is rough. In addition, a new broad peak appears near 1.3 eV, which is attributed to plasmonic effects arising from metallic β-tin inclusions. The plasmon peak disappears in the layers grown at 490°C with the same $SnCl_4$ flow. We conclude that depositing the buffer layer with $SnCl_4$ at low temperatures leads to β-Sn precipitates, where plasmon oscillations can be excited, but are not present for high-temperature growth.

The tin contents in the layers were also estimated by x-ray photoelectron spectroscopy. While XPS measures the total amount of tin in the layers, the presence of substitutional tin in $Ge_{1-x}Sn_x$ alloy buffers is best determined with x-ray diffraction. The (002) diffraction peak is forbidden in pure Ge, because the contributions from the two Ge atoms in the primitive unit cell cancel. It is absent in our buffers grown without $SnCl_4$ or at high temperature. The (004) XRD peak position in these layers is also very similar to pure Ge. The $Ge_{1-x}Sn_x$ (002) peak does appear in buffers grown at temperatures lower than 460°C. From the position of the (004) XRD peak, we can estimate the tin content to be below 7%, ignoring the effects of residual stress. This tin content determined from XRD shifts is much lower than the total tin content of about 20% estimated by XPS. The excess tin is contained in β-tin precipitates, which lead to the plasmonic ellipsometry peaks mentioned earlier.

In summary, the substitutional tin content in thin $Ge_{1-x}Sn_x$ buffer layers grown directly on Si substrates by RPECVD is modulated by temperature and $SnCl_4$ flow rates. Excess tin is present in β-tin precipitates, which lead to plasmonic resonances in ellipsometry spectra.