Awards Convocation and Honorary Lecture
Room Town & Country - Session HL-WeHL

Bunshah Award Honorary Lecture

6:25pm **HL-WeHL-3 R.F. Bunshah Award and ICMCTF Lecture: Some Highlights from over Four Decades of Thin-film Science*, Joe Greene*[1]*,*** University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan **INVITED**

As a graduate student at USC, I was growing epitaxial GaAs(001) films by liquid-phase epitaxy. The layers were of very high purity as demonstrated by Hall and photoluminescence measurements, but we had no techniques sensitive enough to determine the remaining residual impurities. This led me to develop glow-discharge optical spectroscopy (GDOS), the optical analog of modern SIMS. As-deposited films were sputter etched and a spectrometer used to scan the emission peaks arising from the decay of sputtered atoms excited in the discharge. We found that the primary residual impurity was Sn and, via the use of calibration samples (based upon Hall measurements), we determined absolute Sn concentrations (initial detection limit = $3x10^{16}$ atoms/cm^3, 680 ppb). Since then, we, and many others worldwide, have employed GDOS to quantitatively measure dopant diffusion and ion-implantation profiles in III-V, SiGe, and solar-cell absorber layers. GDOS is also used to analyze bulk and thin-film alloys, for real-time process control (film growth rates and thicknesses) during sputter deposition, and for feedback control during high-rate reactive sputtering.

At UIUC, in addition to GDOS, I continued epitaxial semiconductor film growth, but switched to SiGe via UHV-CVD, metastable $(III\text{-}V)_{1-x}(IV_2)_x$ (the "Greene" alloys) by UHV sputter deposition, and GaN by reactive-ion MBE. SiGe CVD was carried out in UHV in order to employ *in-situ* surface-science tools (RHEED, TPD, AES, XPS, UPS, HR-EELS, STM) to investigate atomic-scale growth kinetics. We developed models, with no fitting parameters, to accurately predict Si, $Si_{1-x}Ge_x$, $Si_{1-x}C_x$, and $Ge_{1-x}Sn_x$ film growth rates, compositions, and doping profiles as a function of precursor partial pressures and deposition temperatures. The models are still used worldwide today. The Greene alloys (e.g.: $(GaAs)_{1-x}(Ge_2)_x$) were grown across pseudobinary phase diagrams and exhibited good thermal stability. They have interesting electronic transport, band structure, and phonon properties and are currently used in tunable photodetector and piezoelectric devices. The first high-resistivity single-crystal GaN films, both wurtzite and zincblende, were grown by MBE using evaporated Ga and 35 eV N_2^+ ions. The layers, which had the highest electron motilities yet reported, were used to determine hexagonal and cubic GaN band structures.

Following an invitation to present a Swedish Academy of Science Lecture in the 1980s, colleagues from Linköping University ignited my interest in transition-metal (TM) nitrides (and, recently, TM diborides). The field of nitride hard-coatings was already developing rapidly, but reported properties varied by up to orders of magnitude. Thus, we hoped to make a contribution by growing and measuring fundamental properties of single-crystal compounds and alloys of groups IIIB, IVB, VB, and VIB TM nitrides using tunable magnetically-unbalanced magnetron sputtering which, together with Bill Sproul, Dieter Münz, and Ivan Petrov (all Bunshah Award winners), we developed in 1992. We also demonstrated vacancy hardening, enhanced hardness in superlattices with alternate layers chosen to have large differences in shear moduli, strong electron/phonon interactions, enhanced ductility using alloy design via electronic structure, and self-organized nanostructures. With polycrystalline TM nitrides, we developed a process for real-time control of preferred orientation using high-flux/low-energy ion irradiation and, recently, the growth of fully-dense/low-stress/high-hardness alloys, with no substrate heating, based upon a novel hybrid dc-magnetron/HiPIMS approach. Last year, we were the first to demonstrate controlled B/TM ratios in diboride layers using strong external magnetic fields during magnetron sputtering and controlling pulse lengths, at constant power and frequency, during HiPIMS.

[1] **R.F. Bunshah Awardee**

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