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13. ABSTRACT (Maximum 200 words) Brillouin light scattering (BLS) has been successfully applied to investigate the elastic properties of hard films were studied. The systems investigated include diamond-like-carbon, supported GaN/AlN structures and hard nano-crystalline zirconium-boride films. Highlights of the project include report of the first evidence for the existence of the high frequency longitudinal guided mode (LGM) in a supported hard films (diamond-like-carbon) and emerging evidence for the role of acoustic barriers offered by AlN in localizing elastic waves in GaN films. Preliminary work on amorphous ZrB ₃ films reveals its transformation to hard nano-crystallites of the boride layer with dramatic enhancement of the elastic properties upon high temperature anneal. Analysis of the results was based on calculating the associated elasto-dynamic Green's tensor enabling				
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the local density of states as well as the acoustic mode dispersion(s) to be determined. Observation of the LGM in high-speed films provides a direct means to investigate the longitudinal sound velocity and to determine the C_{11} elastic constant. Thus the LGM, together with the observed shear horizontal and pseudo surface acoustic waves, open new opportunities in the study of high frequency acoustics of laminar structures and coatings that place no limitations on the relative magnitudes of the film/ substrate acoustic velocities.

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Final Report
DAAG 55-97-1-0260

Statement of Problem:

Super hard materials and composites - particularly thin films, coatings and nano-laminates - are finding diverse applications ranging from protective coatings, improved wear at ambient and high temperatures and corrosion resistance. Concurrent with remarkable advances in the synthesis and fabrication of these laminar systems, there is a critical demand for determining their mechanical properties, assessing degrading and developing non-destructive techniques for use over their lifetime.

Ultrasonic echoes are generally ineffective to probe such elastic properties since the associated wavelengths are larger than typical film thickness'. Techniques such as vibrating reed, torsional and bulge testing require detachment of the film from the substrate while nano-indentation suffers from the need that the indentation depth be less than 10% of the film thickness. The latter is also sensitive to the substrate especially for hard films where the yield of the substrate upon indenting the over-layer affects the measurement.

In this project we have developed Brillouin light scattering as an effective technique to probe the elastic properties of hard coatings and wide band gap semiconductor films. This technique is a non-destructive laser scattering process that is sensitive to the acoustic vibrational modes in solids.

Background:

The ability to detect, surface and near surface localized acoustic waves by Brillouin light scattering provided the basis for this work. The technique offers high spatial resolution, and can be readily applied to the study of coatings at high temperatures and in hostile environments.

Acoustic excitations in supported thin films display characteristically different behaviors that depend on the relative magnitudes of the transverse and longitudinal sound velocities in the film and substrate.^{1,2} In the range bounded by the transverse sound velocities of the film (V_F^T) and substrate (V_S^T), the surface Rayleigh and guided Sezawa waves are the primary excitations when $V_F^T < V_S^T$.^{3,4} At higher velocities between the longitudinal sound velocities of the film (V_F^L) and substrate (V_S^L), the longitudinal guided mode (LGM) exists when $V_F^L < V_S^L$, and is characterized by mode displacements primarily along the film plane and a velocity close to V_F^L .⁵ Excitations lying within these two distinct transverse or longitudinal velocity bands provide for a complete description of acoustic waves in a soft film on a hard material (i.e. $V_F^T < V_S^T$).⁶⁻¹⁰ In the opposite limit, i.e. for hard films deposited on soft substrates ($V_S^T < V_F^T$), only one surface acoustic wave (SAW), identified as the Rayleigh wave, exists in a narrow velocity range limited by V_S^T provided the film thickness (h) is below a critical value.¹ Beyond V_S^T this mode transforms into an evanescent pseudo-surface acoustic wave (p-SAW), and eventually approaches the Rayleigh velocity of the film for large h .^{1,11} The presence of only one localized excitation below V_S^T and the weak cross section associated with

higher order modes have attracted few investigations probing the acoustic properties of hard films deposited on soft materials.

Summary of Important Results:

During the early period of this project feasibility studies were carried out to identify the most suitable hard coating layers for Brillouin light scattering. Based on their strong elasto-optic properties, diamond-like-carbon (DLC), which are widely used as hard coatings in a variety of applications, was selected as one of the systems for the initial studies. Subsequently the work has been extended to GaN/AlN structures and hard zirconium-silicon-boride films. In this project we

- reported on the *first successful observation of the longitudinal guided mode (LGM) in hard films*.¹² The discovery was in hard diamond-like carbon films (DLC) supported on silicon. This finding is intriguing since, in this case the guided mode velocity V_{LGM} is greater than both V_s^T and V_s^L , and thus *all* partial waves of this mode can propagate into the substrate.

The DLC films were produced at Lawrence Berkeley Laboratories in the group of O. Monteiro and I. Brown. Hard DLC films with high sp^3 content were studied. The Brillouin light scattering (BLS) measurements were performed in a back scattering geometry at room temperature with a six-pass tandem Fabry-Perot interferometer.^{6,13}

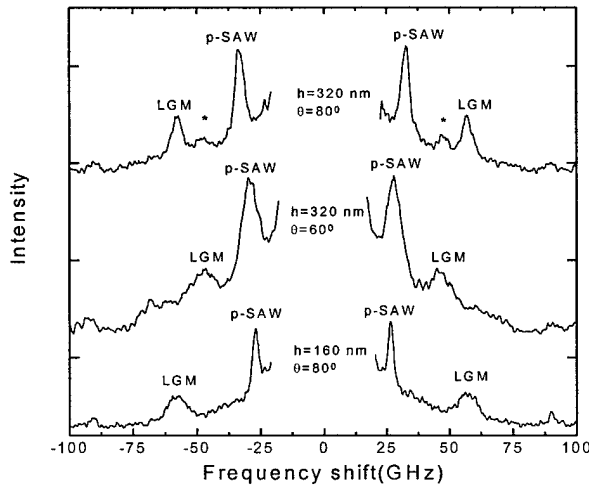


Figure 1: Typical BLS spectra from two DLC films of thickness $h=320$ nm and $h=160$ nm at angles of incidence $\theta = 60^\circ$ and 80° . The strong, lowest frequency (ν_R), peak in each spectrum lying between 26 and 30 GHz is identified as the pseudo-surface wave (p-SAW). The second prominent feature is the LGM and is observed from all films at different angles θ .

- the polarization and phase velocity of the observed LGM were confirmed by calculating, within a Green's function formalism, the local density of phonon states and variations with film thickness.^{12,14} This description allowed for the dispersion of the high frequency LGM as well as that of the SAW and p-SAW excitations to be evaluated. The results are summarized in figure 2.
- Results for the average longitudinal density of states for the DLC layers are shown as a function of frequency in Fig. 3 where θ and h correspond to those values shown in Fig. 1. Two main features are evident. The peak labeled p-SAW with a frequency of ~ 30 GHz relates to the pseudo-surface wave where, for these film thicknesses, at least one of the associated partial waves has an oscillatory component in the substrate. The other prominent feature (LGM) in Fig. 3 relates to the longitudinal guided mode which, in agreement with experiment, shows practically no thickness dependence of its velocity for a given θ . The advantages of such an analysis are several
 - i) the local and integrated density of states (DOS) for each polarization can be analyzed for a given frequency, allowing the relative contribution as well as the spatial distribution of each polarization component to be evaluated.
 - ii) peaks in the integrated DOS for different film thickness' provide for the variation of the phase velocities enabling a direct correlation to the experimental data as illustrated in Fig. 2.
 - iii) prior knowledge of the elasto-optic coefficients are not required to determine mode frequencies via the scattered light intensity.

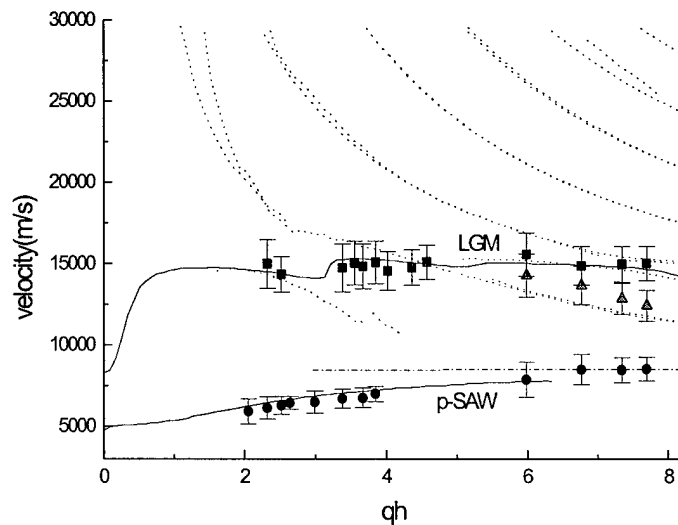


Figure 2: Summary of experimental data, where the filled squares, triangles and circles correspond to the p-SAW, LGM and higher order modes. The lines are calculated velocities.

- iv) the two independent elastic constants ($C_{11} = 614$ GPa; $C_{44} = 244$ GPa) of the DLC layer were directly deduced from the data. The phase velocity of the LGM that is an accurate measure of the longitudinal sound velocity in the film and the known density of the DLC layer gives C_{11} . C_{44} is then deduced from a least-square fit to the experimental dispersion curve of the p-SAW mode.

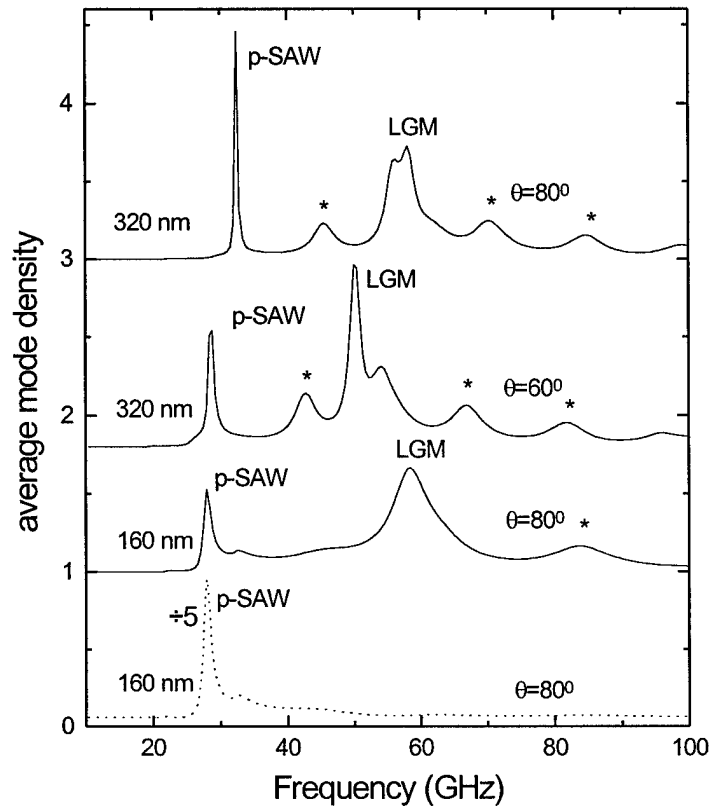


Figure 3: Calculated density of phonon states in DLC for thickness of 160 and 320 nm. The full lines are the longitudinal components, the dotted line the transverse component.

[Note that some of the on-going work on GaN/AlN structures and zirconium-boride films is also being supported by the ARO under the new grant DAAD19-00-1-0396]

- Recent improvements in material processing techniques and contact technology for GaN based material systems have led to rapid progress in the fabrication of GaN opto-electronic and electronic devices.^{15,16,17} The growth of GaN in specific polar directions is also conducive to exploiting their lattice polarization effects that are uniquely suited for applications in high temperature piezo-electronics and as pyroelectric sensors. The growth of GaN

on AlN provides an avenue for the epitaxial growth of the dominant hexagonal GaN polytype onto Si substrates - a highly desirable feature for merging the advantages of the nitride material to the Si-based electronic industry.¹⁸ This important step was recently realized through deposition of either a single AlN layer or AlN/3C-SiC bilayers to grow thick GaN films on Si.¹⁹ *In this project we show that the AlN layer also provides an active, high frequency, acoustic barrier that leads to effective localization of specific guided acoustic excitations to the GaN layer.*

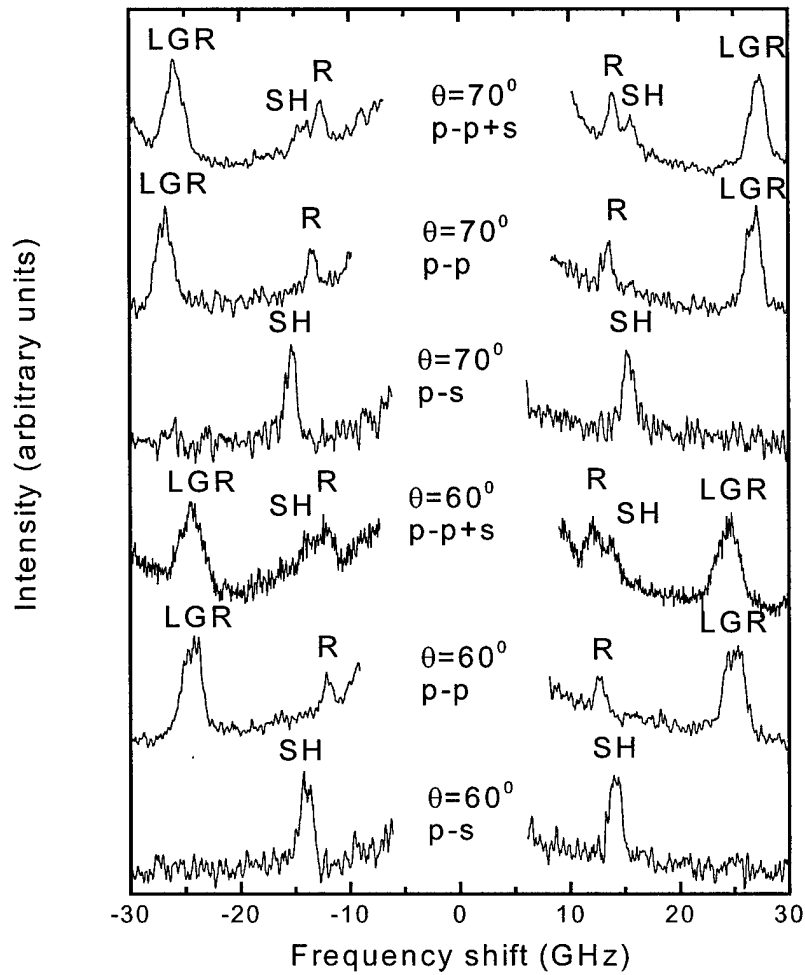


Figure 4: BLS spectra in backscattering from GaN/AlN/SiC/Si for p-p, p-s and p-p+s polarizations. LGR, SH and R identify the longitudinal guided resonance, the shear horizontal and Rayleigh excitations. The single crystal hcp-GaN layer of thickness 1.3 μ m was grown at Purdue University in the group of Professor Melloch on a sequence of designed buffer layers of 3C-SiC (200 nm) and 2H-AlN (200 nm) on Si(111) substrate.

- *Longitudinal guided modes (resonances) GaN/AlN structures.* Figure 4 shows typical polarized (p-p), depolarized (p-s) and unpolarized (p-p+s) Brillouin spectra below 30 GHz from the GaN(1300 nm) /AlN (200 nm) /SiC (200 nm) /Si (111) stack for angle of incidences $\theta = 60^\circ$ and 70° . In addition to the principal Rayleigh mode (R) another mode, identified as the longitudinal guided resonance (LGR) of GaN, is present in the polarized (p-p) spectrum. The low frequency p-s depolarized spectra reveal the presence of the mode labeled SH that corresponds to the in-plane polarized acoustic wave.

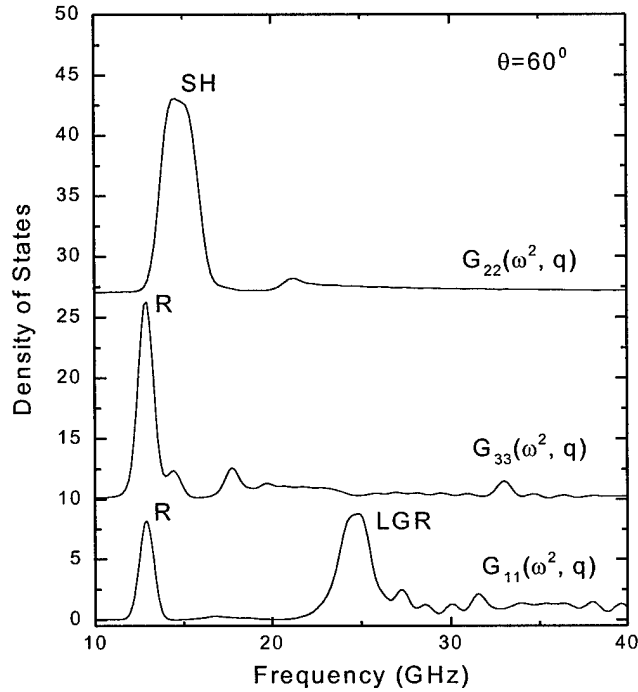


Figure 5: Calculated density of states as a function of frequency for GaN/AlN/Si (111) after convoluting with a Gaussian with a full width at half maximum of 0.3 GHz. The G_{33} and G_{22} are the sagittal and transverse horizontal response function components while G_{11} is the longitudinal component.

- *Shear horizontal guided resonances GaN/AlN structures.* The sharp resonance at 12 GHz in the calculated G_{11} and G_{33} components of DOS (Fig. 5) corresponds to the Rayleigh excitation R observed in p-p scattering. In contrast to the Rayleigh mode there have been only few reports on the observation of the guided shear horizontal excitation that is polarized parallel to the surface,²⁰ as evident in the DOS ($G_{22}(\omega^2, q)$) in Fig. 5. The mode labeled SH (Fig. 4) in the p-s scattering spectra to this excitation. The calculated DOS [$G_{22}(\omega^2, q)$] correctly reproduces this feature (Fig. 5). The

results confirm that at the frequency of the SH mode (14.7 GHz at $\theta = 60^\circ$) there is a strong shear (in-plane) displacement field associated with the wave. The longitudinal displacement component is, by contrast, smaller by several orders of magnitude.

- The character of the LGR and SH modes were determined from the local density of phonon modes $n_i(\omega^2, q, z)$ evaluated within a Green's function formalism.^{12,14} Here i ($=1 - 3$) identifies the mode polarizations where $i = 3, 2$ are, respectively the sagittally polarized transverse and shear horizontal modes and $i = 1$ the longitudinally polarized mode, $\omega (=2\pi\nu)$ the angular mode frequency and z the distance from the film surface where the mode density is calculated. In analyzing the response function of the sample we followed our previous work on DLC discussed above.

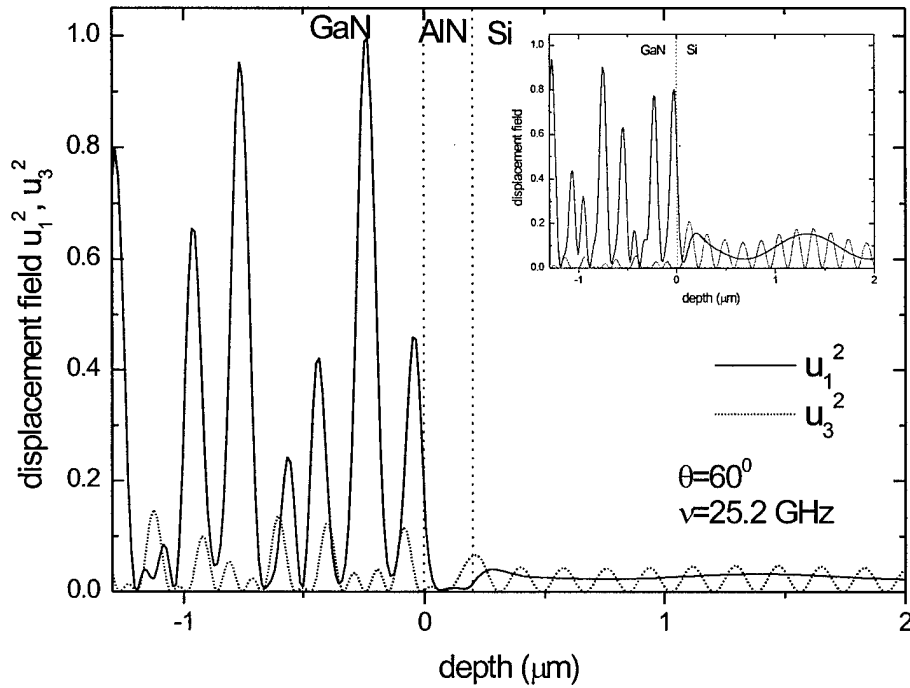


Figure 6: Calculated spatial distributions of the square of the displacement field at 25.2 GHz for the LGR in 1.3 μm GaN film. Full line represents longitudinal component while dotted line is the transverse component. Note localization and polarization of displacement fields inside the film. The inset shows same calculation when AIN layer is removed.

- Figure 6 shows the calculated spatial displacement field (squared) at 25.2 GHz, the frequency of the LGR in the 1300 nm GaN film at $\theta = 60^\circ$. Confirming our assignment of this mode to a guided resonance, the displacements are dominantly longitudinal in character and localized in the GaN film wherein the longitudinal displacement amplitude U_1 attenuates sharply in the AlN layer prior to emerging as a very weak component in the Si substrate. The corresponding shear horizontal and sagittal transverse displacements U_2 and U_3 are significantly weaker than U_1 . The feeble displacement components within the substrate indicate that little mode energy is carried away from the film causing negligible decay of the mode with distance. This localization of the LGR to the GaN layer accounts for its observation as a relatively sharp peak in the Brillouin spectra.
- *High frequency acoustic barriers in GaN/AlN structures:* The inset to figure 6 shows the displacement field in the absence of the AlN layer. In this case, larger displacement fields within the substrate would lead to greater decay in the substrate. The AlN layer minimizes this coupling of partial wave components within the nitride layer with those that radiate energy into the substrate.
- From the variation of the displacement fields with depth it is found that the AlN layer also provides an effective means to localize the SH mode to the GaN layer. We also studied the effect of removing the AlN layer wherein a dramatic decrease in the shear displacement field is again evident near the GaN/Si interface. The profile of the shear displacement field is similar as to when the AlN layer is present. This suggests that either the Si substrate or the AlN intermediate layer can act as effective acoustic barrier to the SH resonance.
- *Elastic constants of GaN.* Spectra recorded at larger free spectral range show peaks associated with the bulk acoustic excitations. In particular the bulk LA mode and weaker TA peak occurs respectively at 71 and 39 GHz. Thus five distinct excitations (the LGR, SHR, Rayleigh mode, bulk LA and bulk TA) are observed in the back scattering geometry from GaN. Given the distinctive polarization features of the two guided modes they directly allow for the elastic constants C_{11} ($=321 \pm 3$ GPa) and C_{66} ($=105 \pm 2$ GPa) to be determined from the mode velocity $[(C_{ij}/\rho)^{1/2}]$. The bulk TA and LA modes allow for a direct determination of $C_{44}=103 \pm 2$ GPa and $C_{33}=342 \pm 2$ GPa via the relations $C_{ii}=(\lambda v/(2n))^2 \rho$. The lack of in-plane anisotropy in the mode frequencies is consistent with the hexagonal symmetry of the GaN surface; the isotropy condition $C_{66} = [C_{11} - C_{12}]/2$ leads to $C_{12} = 111 \pm 2$ GPa.
- *Hard boride films.* Ongoing experiments on zirconium boride films grown on silicon substrates reveal a dramatic enhancement in the C_{11} and C_{44} elastic constants accompanying the conversion of ZrB_3 to nanocrystalline $Zr_{0.9}Si_{0.3}B_{0.3}$ when the films are annealed at high temperatures. These

supported layers are unusual in that the transverse sound velocity of the film and substrate are in near resonance rendering the Rayleigh SAW as the only acoustic mode that is localized to the film. All higher order modes are evanescent. These experiments in progress are being carried out in collaboration with Professors John Kovetakis and Ig Tsong at Arizona State University.

Summary

Brillouin light scattering has been successfully applied to study the elastic properties of hard films. Based on this technique we have presented the first evidence for the existence of the high frequency longitudinal guided mode in a supported hard film. Despite being characterized by evanescent partial waves in the substrate, the LGM is clearly evident as a peak in the BLS spectra. The properties of the new excitation were investigated by calculating the associated elasto-dynamic Green's tensor that allows for the local density of states as well as the mode dispersion to be determined. The findings reported during the course of this project thus provide a major step in classifying long wave acoustic surface and film excitations in supported films that now exhibits equivalence with respect to high frequency acoustics in both hard and soft layers. The observation of the LGM in high-speed films allows for a direct means to investigate the longitudinal sound velocity and therefore to determine the C_{11} elastic constant. Thus the LGM together with p-SAW's that are evident in light scattering experiments now opens new opportunities in the study of high frequency acoustics as well as the elastic properties of laminar structures and coatings which place no limitations on the relative magnitudes of the film/ substrate acoustic velocities.

BLS has also revealed the presence of longitudinal and shear horizontal guided resonances in 2H-GaN films grown on AlN films deposited on Si. Theoretical simulations reveal the properties of these resonances and emphasize the important role of the AlN layer and Si substrate that act as acoustic barriers to these high frequency modes allowing for their localization inside the GaN layer. In addition, bulk LA and TA phonons as well as the surface Rayleigh excitation are observed. Observation of several distinct excitations in a single back-scattering experiment has also allowed for four of the five independent elastic stiffness constants (C_{11} , C_{44} , C_{66} and C_{33}) of the GaN layer to be determined.

The technique of Brillouin scattering is being applied to investigate the elastic properties of hard boride films and the transformations to their structural and mechanical properties that occur upon high temperature anneal. Preliminary results from these ongoing experiments reveal large enhancements in the principal elastic constants of the films when the as-grown ZrB_3 layers transform to nano-crystalline $Zr_{0.9}Si_{0.3}B_{0.3}$.

List of Publications and Technical Reports:

“Elastic properties of diamond like carbon thin films: a Brillouin scattering study”, O.R. Monteiro, I.G. Brown, R. Sooryakumar and M. Chirita, Materials Research Society Symposium Proceedings Volume **44**, 93 1997.

“Observation of guided longitudinal acoustic modes in hard supported layers”, M.Chirita, R. Sooryakumar, Hua Xia, O.R. Monteiro and I.G. Brown, Physical Review B (Rapid Communications) **60**, R 5153 (1999).

“Observation of guided longitudinal acoustic modes and nondestructive characterization of the elastic properties of hard films/ coatings”, M. Chirita, R. Sooryakumar, Hua Xia, O.R. Monteiro and I.G. Brown, AIP Conference Proceedings 497, “Nondestructive Characterization of Materials IX”, Editor Robert E. Green, American Institute of Physics Melville New York 1999, page 473.

“Brillouin light scattering from surface and guided elastic waves”, R. Sooryakumar, M. Chirita, J. Gump, H. Xia, International Advanced Studies Institute Proceedings, ‘Exploration of subsurface phenomena by particle scattering’, Editors N.Q. Lam, C.A. Melendres, S.K. Sinha, IASI Press Maryland, 2000, page 281.

“Acoustic barriers and observation of guided elastic waves in GaN-AlN structures by Brillouin scattering”, M. Chirita, R. Sooryakumar, R. Venugopa, J. Wan and M.R. Melloch, submitted to Phys. Rev. B.

Scientific Personnel:

During the reporting period one student (Mr. Mihail Chirita) was supported as a graduate research assistant. He has completed all requirements for the Ph.D degree and graduated from Ohio State University in August 2000.

In addition, Dr. Hua Xia a post-doctoral associate was supported briefly for three months on this project, while graduate student Mr. Rudra Bandu was supported during a part of the last year of the project.

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