Influence of temperature, strain, alloy composition, doping, and film thickness on the dielectric function of semiconductors

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Due to the pioneering work of Aspnes and Studna [1] and others following their example, the dielectric functions and interband critical point parameters of group IV semiconductors (C, Si, Ge, Sn, SiC) and III/V and II/VI compound semiconductors are fairly well established, as long as we consider these materials in bulk form, free of dopants and impurities, and at room temperature. This talk will give examples of how deviations from these ideal conditions affect the dielectric function and the interband critical points.

(1) With increasing temperature, critical points shift to lower energies and become broader. Also, excitonic enhancements become weaker, leading to a decrease of critical point amplitudes [2].

(2) Biaxial tensile stress (for example in strained epitaxial layers) shifts and splits critical points. These effects can be calculated within continuum elasticity theory using deformation potentials. The weight of the E_1 and $E_1+\Delta_1$ critical point amplitudes may also shift [3].

(3) The critical point energies in relaxed semiconductor alloys (such as $Si_{1-x}Ge_x$ or $Al_{1-x}Ga_xAs$) usually vary continuously, following Vegard's Law with small quadratic bowing corrections. Alloy composition can cause singularities, if the character of the band structure changes, for example a transition from a Ge-like to a Si-like band structure. Alloy scattering as well as statistical or macroscopic fluctuations of composition cause a broadening of the critical points. The amplitudes decrease due to a weakening of the excitonic enhancement. This also affects the excitonic phase angle. In strained semiconductor alloy layers, the effects of stress also have to be taken into account.

(4) Doping has three effects: First, the presence of free carriers adds a small Drude contribution to the undoped dielectric function. Second, the critical points red-shift, broaden, and become weaker due to the screening of the excitonic enhancement by the free carriers and scattering by ionized impurities. Third, due to band filling, the line shape of the critical points may change. We have shown this recently for heavily n-type germanium at low temperatures [4]. This effect can also be seen in transient ellipsometry spectra after femtosecond laser excitation with an 800 nm pump pulse [5].

(5) Finally, we believe that the dielectric function of ZnO varies with film thickness and depends on the choice of substrate. For example, ZnO on quartz is a type-I system, where the excitons are confined leading to an increase of the direct gap absorption. On the other hand, if ZnO thin films are grown on Si, the holes will quickly scatter into the Si substrate, which will lead to a decrease of the near-gap absorption and the refractive index. I hope to have more convincing data by October.

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ELLIPSOMETRIC STUDY ON TiO_2 / ZnO BILAYER LAMINATE FILMS FOR PIEZOELECTRIC APPLICATIONS

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Nanolaminates are multicomponent systems made up of alternating layers of specific materials, each layer being of the nanometre order [1]. Mixing a wide variety of materials makes it possible to fine-tune a material in terms of the films properties, composition and structure [2]. The applications of hybrid films range from solar cells, sensors, piezoelectric MEMS, optoelectronic devices and protective coatings [3], to name only a few. Such suitable materials to be coupled together are zinc oxide (ZnO) and titanium dioxide (TiO_2) due to their close band gap energies, in the range of 3.2 – 3.4 eV [4,5]. Both materials are photocatalysts, ZnO presents a piezoelectric effect and it is interesting to consider how their functionalities will act in a laminate system.

In this work TiO_2 / ZnO bilayer laminate films were deposited on glass and Si (111) substrates by Atomic Layer Deposition (ALD) method, through the spacing and thickness of each layer has been carefully controlled, thus a various combination of TiO_2 and ZnO multilayers were produced. The films were measured by a Woollam™ Rotating Analyzer Ellipsometer and characterized by WVASE® software. We present the ellipsometric results obtained on these laminate films in terms of layer thickness, refractive index and band gap energies, highlighting the influence of composition and layer order on optical and piezoelectric properties.

Keywords: TiO_2 / ZnO laminate films, ALD, ellipsometry, optical /piezoelectric properties

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SPECTROSCOPIC ELLIPSOMETRY STUDY OF HYBRID PEROVSKITE SOLID SOLUTION $FA_xMA_{1-x}PbI_3$ SINGLE CRYSTALS

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Organic-inorganic hybrid perovskites have the generic formula ABX_3 , where X denotes a halide anion and A and B stand for an organic and a metal cation, respectively. These hybrid compounds are semiconductors with highly interesting and tunable properties and are subject of intense research for several applications, mainly in solar cells but also as LEDs and lasers. For all these applications, knowledge of the optical properties is both of fundamental and practical interest. For example, detailed knowledge of the optical constants enables the design and optimisation of light harvesting and out-coupling in the mentioned devices. Tunability of the optical properties may be accomplished by site-substituted solid solutions in A, B, or X sites. In particular, some mixed-cation systems show increased stability for these applications.

In this work, we report on the variation of the optical constants in mixed A-site cation methylammonium (MA) / formamidinium (FA) lead iodide hybrid $FA_xMA_{1-x}PbI_3$ as measured and analysed by spectroscopic ellipsometry in single crystal samples. The detailed structural phase behaviour of the samples is well established [1]. The main result in this work is the analysis of the observed electronic transitions as a function of the composition obtained from fitting the numerically built second derivatives of the dielectric function. The results are discussed together with other optical measurements (e.g., photoluminescence) by relative comparison to the electronic structures of the parent compounds [2,3].

Keywords: Ellipsometry; Hybrid Lead Halide Perovskite; Formamidinium-Methylammonium solid solution; Electronic Structure; Photovoltaics and LEDs

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STEALTH TECHNOLOGY-BASED TERAHERTZ FREQUENCY-DOMAIN ELLIPSOMETRY INSTRUMENTATION

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We present a terahertz (THz) frequency-domain spectroscopic (FDS) ellipsometer design (Fig. 1) which suppresses formation of standing waves by use of stealth technology approaches. The strategy to suppress standing waves consists of three elements: geometry, coating and modulation [1]. The instrument is based on the rotating analyzer ellipsometer principle and can incorporate various sample compartments, such as a superconducting magnet, in-situ gas cells or resonant sample cavities, for example. A backward wave oscillator and three detectors are employed, which permit operation in the spectral range of 0.1–1 THz (3.3–33 cm^{-1}or 0.4–4 meV). The THz frequency-domain ellipsometer allows for standard and generalized ellipsometry at variable angles of incidence in both reflection and transmission configurations. The methods used to suppress standing waves and strategies for an accurate frequency calibration are presented. Experimental results from dielectric constant determination in anisotropic materials, and free charge carrier determination by FDS ellipsometry, and resonant-cavity enhanced optical Hall effect [2] experiments are discussed. Examples include silicon and sapphire optical constants, free charge carrier properties of two dimensional electron gas in group-III nitride high electron mobility transistor structure, and in conductive PEDOT thin polymer films.

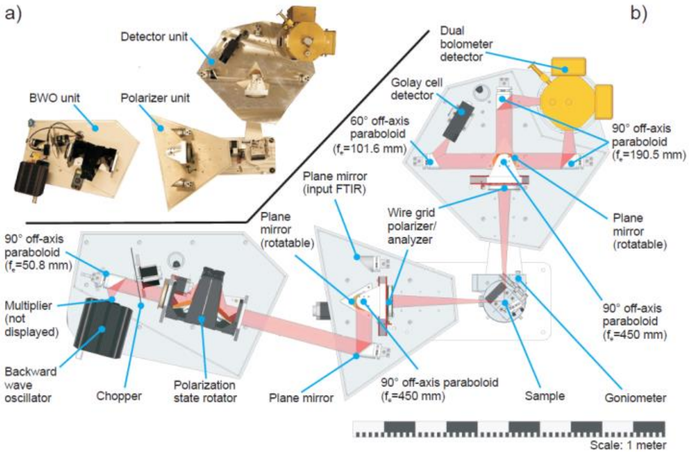

Fig. 1. a) photograph and b) schematic drawing of the THz FDS ellipsometer with major components indicated and without absorbing foam sheets and housing.

Keywords: Terahertz; Stealth technology based;

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QUANTIFYING MOLECULAR INTERACTIONS WITH IR ELLIPSOMETRY

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Molecular interactions play a key role for the structural and functional properties of organic molecules at solid–liquid interfaces. Examples are ordering effects in functionalized thin films, protein aggregation at interfaces, as well as adsorption and desorption behavior of biomolecules on coated surfaces. *In situ* infrared ellipsometry (Fig. 1) accesses both film, analyte, and solvent vibrational fingerprints, and is therefore an advantageous method for measuring said properties. It provides, among other things, insights into film structure, hydration, molecular interactions, and local chemical environments, rendering it a powerful technique for detailed studies of solid–liquid interfaces, particularly of interfaces involving polymers and proteins.

Carbonyl vibrations are versitile infrared reporter modes for probing local chemical environments, that is, solvation effects and specific chemical interactions like hydrogen bonding. We employ *in situ* infrared ellipsometry to investigate structure and interactions of ultrathin polymer films and brushes containing side chain C=O moieties. The focus first lies on rather hydrophilic thermoresponsive, humidity-sensitive poly(*N*-isopropylacrylamide) [PNIPAAm] and poly(2-oxazoline) [POx] brushes whose reversible swelling–dewelling transitions in water are partially driven by a loss of water-interacting C=O groups with increasing temperature.

We then monitor and quantify interface-chromic and hydrogen-bond induced vibrational C=O band shifts of nanometer-thin hydrophobic poly(glycidylmethacrylate) [PGMA] films in contact with different solvents. The tail–train–loop structure of the covalently grafted films potentially influences film–solvent interactions. Using theoretical calculations, we find that effects from solvatochromism and interface geometry are insignificant for aprotic solvents, whereas in water the films' topmost subnanometer layer is involved in hydrogen bonds with H_2O molecules, giving rise to minor but detectable film swelling.

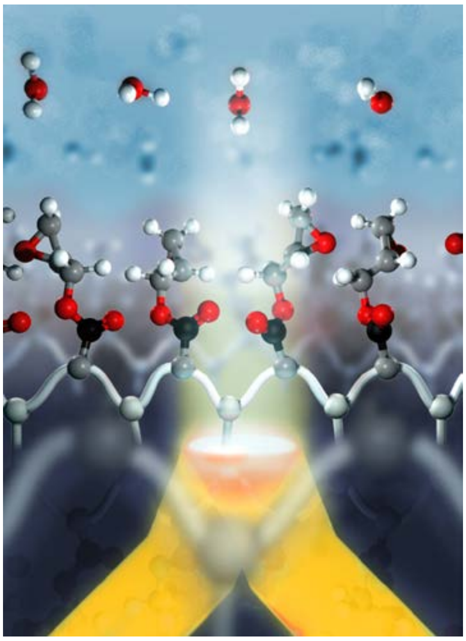

Fig. 1. IR-SE at PGMA–H_2O interface.

Keywords: In situ infrared ellipsometry; Solid–liquid interfaces; Molecular interactions

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