Novel approach to material evaluation of thin surface layers by resonant ultrasound spectroscopy

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Abstract. The laser-based modal resonant ultrasound spectroscopy is modified for measurements of thin surface layers on a substrate. This paper describes determination of all in-plane elastic properties of thin layers from small resonant frequency shifts of substrate induced by deposition of the layer.

1. Introduction

Resonant ultrasound spectroscopy (RUS) is the efficient method for experimental determination of elastic coefficients of anisotropic solids [1]. In this method, information on material elasticity is obtained in a form of resonant spectra of a free-vibrating specimen of the examined material. The sought elastic coefficients are determined inversely, which means that they are tuned such that the calculated eigenfrequencies fit the resonant frequencies identified from experimentally obtained spectrum using an optimizing method.

New quality of the RUS method is obtained by taking into account not only resonant frequencies but also shape of vibration modes for mode identification (modal analysis) and to improve the inversion [2]. The current progress of the RUS method, examples of applications for material characterization of single crystals, various bulk structures, phase transitions are described in [3]. In reference [4], temperature dependencies of elastic coefficients are determined precisely from resonant frequency shifts induced by temperature changes. A technique based on monitoring resonant frequency shifts is generally very sensitive and effective for evaluation of small disturbances [5].

This paper presents possibilities of determination of all in-plane independent elastic coefficients of a generally anisotropic thin surface coating on a known substrate. The proposed approach is based on perturbation theory which enables direct determination of the elastic constants of the surface layer from the shift of resonant frequencies induced by the layer deposition. Fully noninvasive laser based technique is necessary for reliable measurement of such small frequency shifts.

Advantages and limits of the method are shown on evaluation of mechanical properties of DLC (Diamond-Like Carbon) coatings on silicon substrates.
2. Proposed approach

We assume a general unknown anisotropic elastic layer on surface of an anisotropic substrate of known properties. At first, we must solve the forward problem - establish mathematical model of free-vibration of the composed solid and find a numerical solution. The Ritz method is a suitable tool for this purpose [1,3]. Natural approach (3D-Model) stems from vibration of two individual solids with an interface condition, which can be performed by spring-like coupling as it is sketched in Fig.1(a). The elasticity of each of both materials can be described by the Voight form consists of 21 independent coefficients $C_{IJ}$, $I,J = 1,2,...,6$.

If the thickness of layer is much less than the thickness of substrate (Alpha-Model), then its bending can be neglected and all its energy contribution comes from plane stress state (in $w_1$ and $w_2$ directions, see Fig.1(b)). The deformations of the layer follow the surface of the substrate. Hence plane stress coefficients $Q_{ij}$, $i,j = 1,...,3$ (six independent components of the full 3x3 matrix) represent elastic deformation of the thin layer.

![Figure 1: Models of the composed material : layer on substrate](image)

(a) 3D-Model: Two 3D plates with interface conditions (b) Alpha-Model: Thinn layer on substrate

![Figure 2: The upper limit of linearized Alpha-Model which is determined from the comparison with 3D-Model and for 10 percentage error of the frequency shifts](image)

We assume that elasticity $C$ and mass density of the substrate are known and generalized mass $M$ and stiffness matrix $K$ of the substrate alone can be assembled. The resonant frequency shifts related to addition of thin layer on the substrate, can be expressed using first order perturbation theory

$$\delta \omega_i^2 = \frac{\alpha_i^T(\delta K - \omega_0^2 \delta M)\alpha_i}{\alpha_i^T M \alpha_i}$$

(1)

where $\omega_0^2$ are squares of resonant angular frequencies of the substrate ($\delta M = \delta K = 0$), and $\alpha_i$ are corresponding eigenvectors.

Range validity of the asymptotic model (Alpha-Model) can be estimated from comparison with results of numerical solution of the exact formulation of (3D-Model) for the particular example (Si substrate of dimensions: 4x3x0.5mm with diamond layers: $C_{11} = 800, C_{44} = 250$GPa, $\rho = 3.5g/cm^3$). The dependencies of resonant modes (e.g. no. 4 antisymmetrical and...
no. 7 symmetrical) on relative thickness of the layer \( h/H \) where \( H \) is the substrate thickness, are shown in Fig. 2. The validity limit of the (Alpha-Model) was determined for 10 percent frequency shift error.

Once the spectrum of the eigenvibrations is measured and associated, we can reconstruct the parameters of the forward problem to fit the measured data. Left side of the equation (1) can be linearized for small frequency shifts \( \delta \omega_i^2 = \omega_i^2 - \omega_i^0 \approx 2 \omega_i^0 \Delta \omega_i \). Right side of the equation (1) is also linear with respect to coefficients \( Q \) \( (\delta K = \sum_{q=1}^{6} \frac{\partial \delta K}{\partial Q_q} Q_q) \). Therefore we can write our forward problem as a linear equation \( A Q = \Delta f + m_s \) with frequency shifts \( \Delta f \) and elastic constants \( Q \). For any vector of frequency shifts \( \Delta f \) we can easily obtain set of elastic constants \( Q = (Q_1, Q_2,..Q_6)^T \) by inverting the matrix \( A \). Because matrix \( A \) has more rows (it corresponds to number of associated modes) than columns (just 6), we have to use pseudo-inversion

\[
Q = A^{-1}(\Delta f + m_s)
\]

\[
A^{-1} = \text{pinv}(A) = (A^T A)^{-1} A^T
\]

All six elastic constants \( Q \) can be directly determined by eqn. (2). However this simple does not allow us to take into account the material symmetry. When the isotropic properties of the layers is expected, coefficients \( C_{11} \) and \( C_{44} \) must be evaluated by an nonlinear optimization method.

3. Experimental set-up
Full non-contact measurement is provided by thermoelastic excitation of ultrasonic vibration by a focused infrared laser beam (Nd:Yag Pulse Laser System Quantel Ultra with FOLA option; \( \lambda_0 = 1.064 \mu m \), pulse duration 8ns, max. pulse energy 25mJ) guided to the specimen surface via fiber optics, and detection by the scanning laser Doppler interferometer (broadband up to 20MHz). Micro System Analyzer (Polytec, MSA-500), out-of-plane vibration mode, is used for rapid scanning of the laser interferometer beam over very small specimens via microscopic lens. This implementation of laser-ultrasound enables free-standing vibration of the sample, which is placed on a soft supporting matter, and hence reliable and reproducible measurements of frequency spectra.

![Figure 3: Sketch of the experimental arrangement of laser-based resonant ultrasound spectroscopy](image)

4. Specimens
Diamond Like Carbon (DLC) layers were spread on Si substrate plates (orientation [111] and nominal thickness 0.5mm) by Pulse Laser Deposition (PLD) technique in the Institute of Physics ASCR. The regular plate samples for RUS measurements were cut from a center part of the original 10x10mm plates (Tab.1 a). Note that the thicknesses ratios \( h/H \) fulfil the Alpha-Model limit (Fig.2).

5. Measurement and discussion
At first, the Modal RUS measurement was applied to the samples with DLC coatings. After that, the layers were removed by means of butane flame, and the measurements were repeated on the substrates alone. Small frequency shifts \( \Delta f_i \) were evaluated from comparison of
Table 1: Experimental data: samples and results

| Specimen     | Substrate dimensions | DLC Thickness | h/H     |
|--------------|----------------------|---------------|---------|
|              | a [mm]               | b [mm]        | H [nm]  | h [nm] | ±      |
| BIODLC-13-1  | 4.112                | 3.270         | 0.546   | 192    | 5      |
| BIODLC-13-2  | 3.277                | 2.405         | 0.540   | 197    | 5      |
| BIODLC-14-2  | 4.202                | 3.319         | 0.548   | 50     | 5      |

(a) Specimens, dimensions and geometry

| Specimen     | Q11 [GPa]   | Q12 [GPa]   | Q13 [GPa] | Q22 [GPa] | Q23 [GPa] | Q33 [GPa] | C11 [GPa] | C44 [GPa] |
|--------------|-------------|-------------|-----------|-----------|-----------|-----------|-----------|-----------|
| BIODLC13-1   | 778 ± 60    | 187 ± 121   | 0 ± 89    | 778 ± 46  | 0 ± 252   | 296 ± 28  | 865 ± 172 | 295 ± 38  |
| BIODLC13-2   | 692 ± 37    | 97 ± 67     | 0 ± 129   | 692 ± 31  | 0 ± 181   | 297 ± 16  | 711 ± 51  | 297 ± 19  |
| BIODLC14-2   | 904 ± 280   | 205 ± 481   | 0 ± 567   | 904 ± 239 | 0 ± 710   | 349 ± 165 | 990 ± 454 | 349 ± 143 |

(b) Resulting elastic properties of measured DLC layers

both experimental spectra. Approximately 30 resonances in frequency range 0.1-3.2MHz were associated with computed ones and used in determination of Q. An example of the procedure is shown in Fig.4(a) where corresponding parts of spectra (with and without DLC) are shown. From next-by Fig.4(b), we can see quality of the numerical fit of measured \( \Delta f_i \) for elastic constants \( Q \) and following \( C_{11} \) and \( C_{44} \) (Tab.1 b) evaluated by nonlinear inversion assuming isotropic elastic properties of the DLC layers.

![Example (sample BIODLC13-2) of identification, \( \Delta f_i \) determination, and inversion results](image)

Accuracy estimation of obtained elastic constants is based on variance calculation with respect to confidence intervals of determination of frequency shifts and DLC layer thickness. Deviations \( \text{Err}(\Delta f) = 50 \text{Hz} \) were obtained by experimental tests of reproducibility (resolution of frequency was 12.2Hz). Estimated deviation of the DLC layer thickness (±5nm) includes both thickness variations and experimental uncertainty.

The DLC layer of the 50 nm thickness is also measurable, nevertheless greater expected inaccuracies are mainly due to greater relative deviation of the layer thickness.

6. Conclusions
The principle of laser-based modal RUS was suggested for evaluation of mechanical properties of thin surface layers. The method is fully non-contact and without any influence of contact stresses.

It was shown that elastic properties of thin layers (thickness 50nm, layer/substrate thicknesses ratio about \( 10^{-5} \)) are possible to evaluated from small resonant frequency shifts of substrate induced by deposition of the layer. The measurement can determine all six elastic constants in the plane of the layer. Hence in-plane anisotropy can be measured. For the evaluation it
is necessary to measure coating substrate and the same substrate without coating. It can be arranged by measurement the substrate before deposition or remove the layer without damaging or changing the substrate.

Small specimens of several millimeters with defined shape can be used as substrate. More, substrate must exhibit good quality of resonances. Vibration of the layer is driven by the movement of substrate. Thus, by the choice of substrate properties (dimensions, shape, orientation of anisotropy) it is possible to change dynamical deformation of the tested layer.

The suggested procedure has a potential for post-process evaluation of mechanical properties, investigation of functional layers, their responses to external stimuli (temperature, magnetic or electrostatic field) as well as thin coating characterization in-situ during the deposition processes.

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