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<td>計量的な手法の導入とRaman分光測定の応用が電子材料及び関連デバイスの構造解析における新しい可能性を示す。</td>
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<tr>
<td>著者</td>
<td>Giuseppe Pezzotti</td>
</tr>
<tr>
<td>招致</td>
<td>Kyoto University (京都大学)</td>
</tr>
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<td>Giuseppe Pezzotti</td>
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要約

Raman分光測定は、鉱物の構造解析において重要な役割を果たしているが、計量的な手法の導入とRaman分光測定の応用が電子材料及び関連デバイスの構造解析における新しい可能性を示す。特に、電子デバイスの性能評価において、Raman分光測定はその応用が増加している。
An expansion of theoretical principles of Raman spectroscopy towards fully quantitative algorithms for the analysis of electronic materials and related devices

by Giuseppe Pezzotti

Chapter I: INTRODUCTION
A. Main aims and organization of this thesis
B. The Raman spectrum as perceptible expression of quantum effects
C. The quantistically "intrusive" nature of the Raman probe
D. Role of Raman spectroscopy in electronics
   1. Piezoelectrics
   2. Semiconductors

This thesis deals with Raman spectroscopy, which nowadays represents one of the most insightful characterization tools in electronics, and comprehensively suites the technological needs for local and quantitative assessments of crystal structures, domain textures, crystallographic misalignments, and residual stresses in electronic materials and related devices. Recently achieved improvements in data processing and instrumental screening of large sampling areas have provided Raman spectroscopic evaluations with rejuvenated effectiveness, and presently give spin to disciplinarily wider, increasingly deeper and sophisticated experimental explorations. However, besides the continuous expansion of Raman methods in modern science, in this thesis, it is also stressed that the quantum-mechanics aspects of the physics underlying the Raman effect yet remain partly unsolved and actually represent an issue of deep complexity. As a matter of example, yet any applicative development to micromechanical analyses of non-cubic crystallographic structures could be considered as being in its infancy. This thesis revisits some applicative aspects of the quantum physics governing the Raman emission from crystalline matter, in particular exploring the possibility of disentangling the convoluted dependences of the Raman spectrum on crystal orientation and mechanical stress, while preserving their multidimensional (i.e., vectorial and tensorial, respectively) nature in space. Main emphasis is placed on the techno-
logically important class of electronic materials, a matter of great importance in the evolution of our modern society.

Chapter II: FOUNDATIONS OF THE RAMAN THEORY
A. The quasi-particle approach to the Raman effect in crystalline solids
B. Raman scattering tensors vs. polarizability tensors
C. Group theory and the manifold role of crystal symmetry
D. Irreducible representations
   1. The tetragonal structure of barium titanate
   2. The trigonal structure of lithium niobate
   3. The monoclinic structure of lead niobate titanate
   4. The hexagonal wurtzitic structure of gallium and aluminum nitrides
E. Raman tensors and their tensor elements
F. Strain tensors and the Raman spectrum: secular equations
G. Computational approaches in applied Raman spectroscopy

This is a tutorial chapter to introduce the overall Raman effect and, in particular its description in terms of symmetry and group theory. From the one side, it is described how the main target of both theoretical and experimental assessments in this thesis resides in the analysis of piezoelectric and semiconductor compounds with non-cubic crystallographic structures. For these important classes of materials, working algorithms are newly and explicitly worked out in order to quantitatively extract both structural and mechanical information from polarized Raman spectra. From the other side, a number of studied crystal structures are described with starting from general principles of symmetry and ending to the respective description of their vibrational modes. Derivations and explanations of the Raman selection rules (tensor elements) and secular equations are finally given for each studied compound. Moreover, a miscellaneous description of computational approaches and mathematical tools is given, as it has gradually become available in modern physics research.

Chapter III: RAMAN PROBE, SPECTROSCOPIC EQUIPMENT AND SOFTWARES
A. Statistic and deterministic approaches to probe analysis
B. Structure and geometry of the Raman probe
C. Raman equipment and software packages
D. Quantitative Raman probe calibrations of electronic materials

This chapter offers a thorough analysis of the sample/probe interaction in the case of both through-focus and confocal Raman probe for all the electronic materials of interest in this thesis. Probe response functions are explicitly derived and basic parameters listed for a direct application of
Chapter IV: RAMAN SELECTION RULES AND THEIR EXPERIMENTAL VERIFICATION
A. Extension of the Raman selection rules
B. Raman tensor parameters for different crystal structures
   1. Tetragonal structure
   2. Trigonal structure
   3. Hexagonal wurtzite-like structure
   4. Monoclinic structure

The complex and differentiated Raman responses of a number of crystal structures to their local crystallographic orientation are comprehensively rationalized and described in this chapter, according to a formalism unified for all the studied crystallographic structures. This chapter also includes quantitative calibrations and verifications of the Raman selection rules derived in Chapter II.

Chapter V: SECULAR EQUATIONS AND THEIR EXPERIMENTAL VERIFICATION
A. Definitions and adopted formalism
B. Secular equations and PDP constants
   1. Tetragonal structure
   2. Trigonal structure
   3. Hexagonal (wurtzitic) structure

The different Raman spectroscopic responses of various crystal structures to the presence of a general strain tensor in the lattice are studied in this chapter. The anisotropic strain behaviors of different electronic materials at the molecular scale are comprehensively rationalized and described, according to an unified formalism for all the studied crystallographic structures, and including quantitative calibrations and verifications of the Raman secular equations derived in Chapter II.

Chapter VI: ORIENTATION DISTRIBUTION FUNCTIONS FOR STATISTICAL ANALYSES IN THE PROBE VOLUME
A. The ODF statistical approach
B. Definitions and adopted formalisms for statistical texture analysis
C. Stress analysis in partially textured structures
This chapter describes an additional and newly developed mathematical tool, which was needed for translating the worked out spectroscopic algorithms from single-crystalline to polycrystalline (i.e., partly textured) materials. This mathematical tool is represented by a statistical description of domain textures based on the orientation distribution functions, as they were built up by means of a polynomial expansion of Wigner functions in the three Euclidean dimensions.

Chapter VII: APPLICATIONS OF RAMAN SPECTROSCOPY TO THE ANALYSIS OF PIEZOELECTRICS AND SEMICONDUCTORS
A. Microscopic analyses of three-dimensional domain patterns and tensor-resolved residual stresses in tetragonal BaTiO$_3$ and trigonal LiNbO$_3$ single-crystals
B. In situ study of the effect of annealing on domain texture in a-plane-indented BaTiO$_3$ single crystal
C. Microscopic analyses of three-dimensional domain patterns and tensor-resolved residual stresses in MLCC devices
   1. Domain textures and residual stress issues in MLCC devices
   2. Domain textures and their spatial distributions in MLCC
   3. Three-dimensional residual stress distributions in MLCC
   4. Linking domain textures and residual stress state to functional parameters
D. Reliability assessments of crystal orientation in LiNbO$_3$ substrates
   1. Structural issues related to LiNbO$_3$-based devices
   2. Quantitative Raman analyses of crystallographic homogeneity and residual stress tensor in SAW substrates
E. Monoclinic PMN-PT single-crystals with compositions within the morphotropic phase boundary
   1. Structural and functional characteristics of solid solutions near the morphotropic phase boundary
   2. Topological visualization of different monoclinic phase structures and orientations in PMN-PT single-crystals
F. Responses of GaN and AlN wurtzitic film structures to processing parameters in terms of crystal orientation and residual stress gradients
   1. Crystallographic distortion assessments in wurtzitic GaN films grown on sapphire substrates
   2. Three-dimensional tensor-resolved stress analyses in wurtzitic GaN films grown on sapphire substrates
   3. Statistical assessments of crystal homogeneity and residual stresses in nominally (0001) wurtzitic AlN film grown on (001)Si for WCDMA filters
The entire body of spectroscopic and computational achievements obtained in the previous six chapters of this thesis is interpreted in this applicative chapter as a means for assessing both crystallographic textures and stress-related issues in the three-dimensional space (thus preserving their vectorial and tensorial nature, respectively), and extensively applied through a number of working examples based on the crystallographic and micromechanical analyses of real electronic devices. Such systematic characterizations of electronic materials and devices not only vividly represent a direct application of the newly developed equations, but also solve some long-standing technological issues, like as the effect of residual stresses on both structural reliability and functionality of multilayer ceramic capacitors and the mm-scale (i.e., in toto) evaluation of crystallographic homogeneity of piezoelectric wafers and modern film components made of advanced semiconductor compounds.

Chapter VIII: CONCLUSION AND FUTURE PERSPECTIVES
A. Developing Raman spectroscopic standards in electronics
B. Analytical requirements and future trends in Raman spectroscopy

In this final chapter, the overall achievements of this thesis are summarized and a perspectival bird-eye view offered, which stigmatizes both the present state and the expected future developments of quantitative Raman spectroscopy. This latter discussion also includes current aspects related to the development and evolution of the Raman device. In substance, this thesis aims at providing rigorous spectroscopic foundations to Raman approaches dealing with the analyses of non-cubic crystals. It should also provide long missing pieces in the complex field of quantitative Raman spectroscopy, and thus could represent a substantial step ahead in designing new electronic devices with improved functional behavior and structural reliability.

Appendix A: A SHORT TUTORIAL ON GROUP THEORY AND SPACE GROUPS IN REAL AND RECIPROCAL SPACES
Appendix B: PHONON DISPERSION EFFECTS
Appendix C: ANISOTROPY OF YOUNG’S MODULUS AND POISSON’S RATIO

These three tutorial appendices, which are attached to the end of the thesis, deal with group theory, phonon dispersion, and anisotropy of elastic constants, respectively. They give some tutorial information, which could facilitate the comprehension of the mathematical and physical aspects of the somewhat cumbersome algorithms presented throughout this thesis.