

# Contents

|  |           |
|--|-----------|
| Abstract .....   | 9         |
| Streszczenie .....   | 10        |
| Glossary of symbols .....  | 11        |
| List of acronyms .....   | 15        |
| Acknowledgement .....  | 17        |
| <b>1. Introduction .....</b>   | <b>19</b> |
| <b>2. Basic properties of titanium dioxide .....</b>                       | <b>22</b> |
| 2.1. Crystallographic structure .....                                      | 22        |
| 2.2. Electronic band structure and optical properties .....                | 27        |
| 2.2.1. Band structure of $\text{TiO}_2$ .....                              | 29        |
| 2.2.2. Optical properties .....  | 33        |
| 2.3. Electrical properties and defect structure .....                      | 34        |
| 2.3.1. Nonstoichiometry in rutile .....                                    | 35        |
| 2.3.2. Electrical conductivity and point defect structure .....            | 35        |
| 2.3.3. Transport mechanism of charge carriers .....                        | 38        |
| <b>3. Applications .....</b>   | <b>42</b> |
| 3.1. Gas sensors .....   | 42        |
| 3.1.1. Classification and basic parameters .....                           | 42        |
| 3.1.2. Resistive gas sensors .....   | 46        |
| 3.1.2.1. Gas sensing “surface” mechanism .....                             | 47        |
| 3.1.2.2. Gas sensing materials and devices .....                           | 49        |
| 3.2. Nonlinear optical devices .....                                       | 52        |
| 3.2.1. Nonlinear optical polarization and susceptibility .....             | 52        |
| 3.2.2. Optical Kerr effect .....   | 54        |
| 3.2.3. Basic applications of nonlinear optical phenomena .....             | 55        |
| <b>4. Nonstoichiometric <math>\text{TiO}_{2-y}</math> thin films .....</b> | <b>61</b> |
| 4.1. Deposition of $\text{TiO}_{2-y}$ thin films .....                     | 62        |

|  |            |
|--|------------|
| 4.1.1. Rf sputtering .....   | 63         |
| 4.1.2. PEC dc magnetron sputtering .....   | 65         |
| 4.2. Determination of the departure from stoichiometry $y$ .....                           | 68         |
| 4.2.1. RBS .....   | 68         |
| 4.2.2. NRA .....   | 72         |
| 4.2.3. XPS .....   | 75         |
| 4.3. Microstructure evolution as a function of the process parameters .....                | 80         |
| 4.3.1. Experimental results .....  | 81         |
| 4.3.1.1. X-ray diffraction .....   | 81         |
| 4.3.1.2. Grazing Incidence X-ray Reflectivity (GIXR) .....                                 | 91         |
| 4.3.1.3. TEM .....   | 94         |
| 4.3.1.4. AFM .....   | 98         |
| 4.4. Optical properties of $\text{TiO}_{2-y}$ thin films .....                             | 99         |
| 4.4.1. Transmittance and reflectance of a thin film .....                                  | 101        |
| 4.4.2. Spectrophotometry .....   | 105        |
| 4.4.2.1. Experimental .....  | 105        |
| 4.4.2.2. Results .....   | 108        |
| 4.4.3. Ellipsometry .....  | 120        |
| 4.5. Electrical properties of $\text{TiO}_{2-y}$ thin films .....                          | 126        |
| 4.6. Discussion .....  | 130        |
| 4.7. Conclusions .....   | 132        |
| <b>5. Gas-sensitive resistors based on modified titanium dioxide</b> .....                 | <b>134</b> |
| 5.1. Elaboration of gas-sensitive materials .....  | 135        |
| 5.2. Chemical composition .....  | 136        |
| 5.3. Crystallographic structure .....  | 139        |
| 5.3.1. Experimental results on $\text{TiO}_2\text{:Cr}$ and $\text{TiO}_2\text{:Nb}$ ..... | 141        |
| 5.3.2. Experimental results on $(\text{Ti, Sn})\text{O}_2$ .....                           | 143        |
| 5.4. Morphology and light scattering experiments .....                                     | 145        |
| 5.4.1. Experimental results on $\text{TiO}_2\text{:Cr}$ and $\text{TiO}_2\text{:Nb}$ ..... | 146        |
| 5.4.2. Experimental results on $(\text{Ti, Sn})\text{O}_2$ .....                           | 149        |
| 5.5. Electronic structure from XPS and optical measurements .....                          | 153        |
| 5.5.1. Experimental results on $\text{TiO}_2\text{:Cr}$ and $\text{TiO}_2\text{:Nb}$ ..... | 153        |
| 5.5.2. Experimental results on $(\text{Ti, Sn})\text{O}_2$ .....                           | 156        |
| 5.6. Electrical properties .....   | 159        |
| 5.7. Gas-sensor application .....  | 162        |
| 5.7.1. Theoretical models of the gas-solid interaction .....                               | 163        |
| 5.7.1.1. Surface interaction .....   | 163        |
| 5.7.1.2. Bulk interaction .....  | 163        |

|  |            |
|--|------------|
| 5.7.2. Experimental results on $\text{TiO}_2\text{:Cr}$ and $\text{TiO}_2\text{:Nb}$ ..... | 164        |
| 5.7.3. Experimental results on $(\text{Ti, Sn})\text{O}_2$ .....                           | 167        |
| 5.8. Conclusions .....   | 175        |
| <b>6. Titanium dioxide-noble metal nanocermet for photonic devices .....</b>               | <b>178</b> |
| 6.1. Preparation of thin films .....   | 179        |
| 6.2. Chemical composition .....  | 179        |
| 6.3. Microstructure .....  | 182        |
| 6.4. Linear optical properties .....   | 190        |
| 6.4.1. Theoretical background .....  | 190        |
| 6.4.2. Experimental results .....  | 198        |
| 6.5. Nonlinear optical properties .....  | 201        |
| 6.6. Conclusions .....   | 205        |
| <b>7. Summary and outlook .....</b>  | <b>207</b> |
| References .....   | 209        |