SEMI MF1389-1115 (Reapproved 0222)
TEST METHOD FOR PHOTOLUMINESCENCE ANALYSIS OF SINGLE CRYSTAL SILICON FOR III-V IMPURITIES

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NOTICE: The section symbol (§) is used to reference a numbered section, paragraph, or header and all subordinate paragraphs, headers, and embedded material (i.e., EXCEPTIONs, lists) therein. The paragraph symbol (¶) is used to reference a particular numbered paragraph and embedded material therein. When duplicated (i.e., §§ and ¶¶) the symbols are used to reference more than one section or paragraph, respectively.

1 Purpose

1.1 Electronic-grade polycrystalline silicon producers and users require information regarding impurities for quality assurance as well as for research and development purposes. Polysilicon is float-zoned and a sample from the zoned rod is analyzed following this Test Method to obtain impurity densities that can be related to the impurity content of the starting material (refer to SEMI MF1723).

1.2 Photoluminescence analysis identifies and quantifies the electrically active dopant impurities in monocrystalline silicon. This Test Method addresses boron, phosphorus, arsenic, and aluminum, found as impurities in electronic grade silicon.

1.3 This Test Method can be applied to doped and undoped float-zoned or Czochralski material.

2 Scope

2.1 This Test Method covers the simultaneous determination of electrically active boron, phosphorus, arsenic, and aluminum content in low-dislocation monocrystalline silicon.

NOTE 1: These chemical species can also be determined by the low temperature infrared analysis procedure of SEMI MF1630.

2.2 This Test Method can be used for samples that have dopant densities between approximately 1×10^{11} and approximately 5×10^{15} atoms/cm^3.

2.3 The concentrations obtained using this Test Method is based on an empirically determined relationship of the logarithm of the concentration to the logarithm of specific luminescence line-intensity ratios.

2.4 The empirical relationship established assumes a constant sample excitation level for all measurements on a given instrument.

2.5 To accommodate differences in instrumentation, two methods are included. Test Method A refers to procedures appropriate for dispersive infrared spectrophotometers operating under the high sample excitation conditions and Test Method B refers to procedures appropriate for Fourier transform instruments operating under low excitation conditions.

2.5.1 Typical calibration curves for each test method are provided. These curves are modified for each instrument using the analysis of standard samples as reference data. Once modified, the curves for a given instrument should produce sample dopant density values that agree with other similarly operated instruments using the same test method. Data obtained using Test Method A may not agree with data obtained using Test Method B, hence values must be reported with reference to the test method used.

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NOTE 2: Several different methods of photoluminescence analysis are currently in practice worldwide. These test methods address two of these, one (Test Method A) in use primarily in Japan[1] and the other (Test Method B) primarily in the United States. Recently published works[2,3] describe other approaches.

2.6 Many laboratories use photoluminescence to analyze epitaxial layers. However this application encounters many variables and the underlying physics is not fully understood; hence these test methods do not attempt to outline standard practices regarding such analysis.

NOTICE: SEMI Standards and Safety Guidelines do not purport to address all safety issues associated with their use. It is the responsibility of the users of the Documents to establish appropriate safety and health practices, and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 *Variations in Excitation Intensity* — The extrinsic bound exciton (BE) and intrinsic free exciton (FE) luminescence features do not vary at the same rate with excitation intensity.[4] The FE features increase proportionally with excitation intensity, while the BE features increase proportionally at low excitation levels but become more slowly increasing at higher excitation levels generally above the electron hole droplet (EHD) onset point. Since the calculated concentrations are derived from the ratio of extrinsic features to the intrinsic feature, the ratio will be decreasing as the excitation intensity is increasing. Thus, if a sample is measured at a higher excitation level than the instrument is calibrated for, the calculated concentration will be artificially low, and vice versa.

3.2 Sample surface damage, bulk defects, or other lifetime reducers also affect the line-intensity ratios and overall luminescence intensity owing to their tendency to reduce the steady state population of excitons, thus mimicking the effects of a lower excitation intensity. Other mechanisms related to the presence of these defects may also introduce decalibrating effects. Some luminescence features are generated by defects; for example, those at 6510 and 7050 cm^{-1} are typical of thermally stressed samples. Such features can provide qualitative information about the presence of defects.[5,6]

3.3 The ratios and line widths of the silicon luminescence features vary strongly with temperature, hence variations in sample temperature must be avoided. Corrections for the effects of temperature variations are included in these test methods (refer to ¶ 7.1).

3.4 *Overlapping Spectral Features*

3.4.1 The boron B_{TO}(BE) feature at 8812.6 cm^{-1} overlaps the $P_{TO}(b'_1)$ feature at 8812.7 cm^{-1} causing a direct error when calculating boron concentration. The beta-series $P_{TO}(b'_1)$ line is approximately one-tenth the intensity of the alpha series P_{TO}(BE) line at 8806.6 cm^{-1}, so a subtraction based on the amount of phosphorus present can be made in the boron feature measurement. An alternative approach is to use the $B_{TO}(b_1)$ boron line, which is free from a coincident phosphorus line, provided the instrument has been calibrated for this feature.

3.4.2 The antimony Sb_{TO}(BE) line falls between the boron and phosphorus transverse optical (TO) features. Since the line widths are broad relative to the line positions of these features, the presence of antimony affects the apparent intensities of boron and phosphorus TO features. The no-phonon, (NP) features for these elements could be used providing the instrument is calibrated for them.

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[1] Test Method A is essentially equivalent to JIS H 0615, Test Method for Determination of Impurity Concentrations in Silicon Crystal by Photoluminescence Spectroscopy. This standard is available from Japanese Standards Association, 4-1-24 Akasaka, Minato-ku, Tokyo 107-8440, Japan; Telephone: +81.3.3583.8005, Fax: +81.3.3586.2014, http://www.jsa.or.jp

[2] Colley, P. McL., and Lightowlers, E. C. "Calibration of the Photoluminescence Technique for Measuring B, P, and Al Concentrations in Silicon in the Range 1e12 to 1e15 at/cm^3 Using Fourier Transform Spectroscopy." *Semiconductor Science and Technology* (1987): pp. 157–166.

[3] Schumacher, K. L., and Whitney, R. L., *J. Electron. Materials* (1989): pp. 681–687.

[4] Nakayama, H., Nishino, T., and Hamakawa, Y. "Analysis of the Excitation Luminescence of Silicon for Characterization of the Content of Impurities." *Jap. J. Appl. Phys*. (1980): pp. 501–511.

[5] Drozdov, N. A., Patrin, A. A., and Tkachev, V. D. "Recombination Radiation on Dislocations in Silicon." *Soviet Physics, J .Experimental and Theoretical Physics* (1976): p. 597.

[6] Suezawa, M., Sasaki, Y., Nishina, Y., and Sumino, K. "Radiative Recombination on Dislocations in Silicon Crystals." *Jap. J. Appl. Phys.* (1981): L537.

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3.4.3 In general, the broad TO phonon region features can interfere, particularly when a sample contains widely differing levels of impurities. For example, when boron greatly exceeds phosphorus, the P_{NP}(BE) line must be used, and when phosphorus greatly exceeds boron, one of the approaches described in ¶ 3.4.1 must be used.

3.5 Stress in samples can cause NP region feature splitting and thus affect the established TO/NP line ratio for a given impurity. The concentrations calculated from such spectra would be artificially low. Peak area calculation methods reduce the measurement's sensitivity to line splitting effects.

3.6 The calibration curves presented in these test methods are traceable to resistivity measurements (refer to SEMI MF723), neutron transmutation doped, (NTD) reference material, and low-temperature infrared absorption spectroscopy (FT-IR) measurements (as a secondary standard) (refer to SEMI MF1630). Hence inaccuracies in the work that produced the calibration curves impact the accuracy of the PL results.

4 Referenced Standards and Documents

4.1 *SEMI Standards and Safety Guidelines*

SEMI C28 — Specification for Hydrofluoric Acid

SEMI C30 — Specification for Hydrogen Peroxide

SEMI C35 — Specification and Guide for Nitric Acid

SEMI M59 — Terminology for Silicon Technology

SEMI MF723 — Practice for Conversion Between Resistivity and Dopant or Carrier Density for Boron-Doped, Phosphorus-Doped, and Arsenic-Doped Silicon

SEMI MF1630 — Test Method for Low Temperature FT-IR Analysis of Single Crystal Silicon for III-V Impurities

SEMI MF1723 — Practice for Evaluation of Polycrystalline Silicon Rods by Float-Zone Crystal Growth and Spectroscopy

4.2 *ASTM Standards*[7]

ASTM D5127 — Standard Guide for Ultra-Pure Water Used in the Electronics and Semiconductor Industries

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 Acronyms, terms, and symbols related to silicon technology are listed and defined in SEMI M59.

5.2 *Other Definitions Used in this Standard*

5.2.1 *defect luminescence lines* — those features arising from defect structures in the silicon.

5.2.2 *electron hole droplet (EHD)* — the condensed phase (liquid) of the excitonic gas generated by photoexcitation.

5.2.2.1 *Discussion* — The exciton population is dependent upon excitation intensity and can be raised to the point where the exciton density is sufficient to allow condensation of the exciton gas into a liquid like exciton state.[8] The existence of EHD luminescence can be an indirect measurement of excitation power density on the sample.

5.2.2.2 EHD onset occurs at the point in the sample excitation intensity curve where the electron-hole-droplet begins to form.[9] The EHD luminescence includes a very broad feature underlying the TO region impurity lines which, with increasing excitation intensity, both intensifies and shifts to lower energies relative to the other silicon luminescence features.

5.2.3 *excitons* — the electron-hole pairs that give rise to the luminescence of interest upon recombination at either a free lattice site (free exciton) or an impurity atom site (bound exciton).

[7] ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, USA; Telephone: +1.610.832.9585, Fax: +1.610.832.9555, http://www.astm.org

[8] Nakashima, H., and Shiraki, Y. "Role of Shallow Impurities and Lattice Defects in Nucleation of Electron-Hole Droplets in Si." *Solid State Comm*. (1981): pp. 195–197.

[9] Hammond, R. B., and Silver, R. N. "Onsets of the Electron-Hole Droplet Luminescence in Si." *Phys. Rev. Lett.* (1979): pp. 523–526.

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