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Budapest University of Technology and Economics  
Faculty of Electrical Engineering and Informatics

# **Semitransparent monocrystalline silicon solar cell technology and characterization**

**Ph.D. Thesis booklet**

Author: Földváry-Bándy Enikő

Advisor: Prof. Dr. Rencz Márta, D.Sc.

**Department of Electron Devices**

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# 1. Introduction

In today's growing energy needs we focus our attention on renewable energy sources. Building integrated photovoltaics are an attractive concept for economic generation of solar power. By simultaneously serving as building envelope material and power generator, BIPV<sup>1</sup> systems can assure savings in materials and electricity costs. Integration of semitransparent solar cells into windows opens the prospect of employing the entire facade of a building for solar power generation purposes, rather than simply employing the limited roof space. Several semitransparent photovoltaic technologies are suitable for semitransparent facade and solar window applications, but semitransparent crystalline silicon solar cell structures compared to thin film have a higher performance and also a mature technology. The building integrated photovoltaic market is in front of a substantial growth between now and 2019, according to Transparency Market Research's latest findings. Monocrystalline silicon technology receives substantial attention and demand, by today it holds more than 60% of the market share.

Looking at industrial semitransparent crystalline silicon solar cells, many options are available on the market to achieve the desired transparency. Firstly, a popular solution for regulating the transmitted light intensity is to place the non-transparent cells at a certain distance from each other. Secondly, technology induced semitransparency can be established by locally removing the silicon material. Two major industrial production processes were employed for the creation of the through-holes in silicon solar cells: laser cutting and mechanical grinding. By using laser technology, square recesses can be cut to produce the required light transparency. Fabrication of semitransparent solar cells with the mechanical grinding method was stopped in the industrial environment due to extensive breakage of the solar cells.

## 2. Research aims and objectives

Specific problems arise when laser micromachining is adopted for crystalline semiconductors, in particular when cutting is done on completed

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<sup>1</sup> Building integrated photovoltaics

devices. According to this, my research goal was to work out an alternative through silicon hole creation method, which can be used for the manufacturing of semitransparent monocrystalline solar cells. The objective was to lay down the foundation for a state of the art bifacially active semitransparent n-type silicon based solar cell technology, and to manufacture experimental devices. Compared with the solutions available in the industrial manufacturing process, the through-holes that ensure the desired transparency level of the solar cells can be realized using anisotropic metal ion free TMAH<sup>2</sup> bulk micromachining technology. The tasks that had to be fulfilled were centred on the analysis of the applicability and integrability of such a technological step in the solar cell technology and optimization of the etching process considering different etching parameters. Another key aim of the research was to study the masking layer growth possibilities, their integration into the solar cell process and analyse the masking properties of the layers. Knowing the selectivity of the etchant for the masking layers and considering the heat load associated with the growth process, the optimized masking layer can be chosen.

In addition to the tasks listed above, in order to enhance the efficiency of the solar cell, a reflectance reduction technology needed to be worked out and incorporated into the manufacturing. For this reason, surface texturing experiments with TMAH etchant were conducted and the etching parameters optimized in order to get the lowest average reflectance, best homogeneity and pyramidal coverage of the silicon surfaces. To further decrease the surface reflectance silicon oxynitride antireflection coating deposition method was also studied.

Besides reliable etching processes, for a working energy converting device it was essential to develop technological processes for the creation of the emitter, the BSF and the contact layers. During my research, the goal was to work out and analyse layer structures and layer processing steps that can be the base for a semitransparent monocrystalline silicon solar cell technology and are compatible with the processes used in industrial manufacturing or research.

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<sup>2</sup> Tetramethylammonium hydroxide

### 3. Applied tools and inspection methodologies

The infrastructural background of my work was provided by the Semiconductor Laboratory of Department of Electron Devices - BME, which was located in the Building V2. The laboratory has moved to the Building Q where it was completely rebuilt, so the technological possibilities were expanded. Mostly all the solar cell technology related work was carried out in the new clean room of the department.

The processing technology I have elaborated for the semitransparent solar cell consists of 5 complex work phases. For the implementation I used the available equipment in the laboratory (precision balance, photolithography and wet processing toolsets, tube furnaces for the high temperature processes, vacuum evaporator, RF sputtering equipment, screen printer machine, RTP<sup>3</sup>, dicing equipment). The etching experiments were carried out with a new experimental setup. I also cooperated with other laboratories to broaden the range of available tools for certain technological steps of my work. The fellows of MTA EK MFA<sup>4</sup> Microtechnology Department helped with masking layer deposition processes, while the fellows of Exasol Kft did the laser cutting processes.

I have examined the deposited layers, obtained surfaces and finished devices with several different methods. The minority carrier lifetime of the raw material was mapped with  $\mu$ PCD<sup>5</sup> method. The thickness of the thin layers was measured with mechanical profilometer and ellipsometer. During the experimental research of the through-hole creation process, the depth of the trenches was measured with mechanical dial indicator. The inspection of surface morphological properties and layer defects was carried out by usage of optical microscopy and scanning electron microscopy. The captured images were further analysed with an image processing program. The reflectance of the surface containing pyramidal structures and antireflection coating was determined with spectrophotometer. The antireflection coatings were examined with ellipsometer and XPS<sup>6</sup> measurements. During my research, I have also used a program suitable for thin film optical coating design and analysis.

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<sup>3</sup> Rapid thermal processor

<sup>4</sup> MTA Institute of Technical Physics and Materials Science

<sup>5</sup> Microwave induced photoconductive decay

<sup>6</sup> X-ray photoelectron spectroscopy

The resistivity of the doped layers was measured with four point probe method, while the doping profile was determined with spreading resistance measurements. The electrical parameters of the completed devices were determined by J-V characteristic measurements, vibrating capacitor surface potential mapping and thermal behaviour testing.

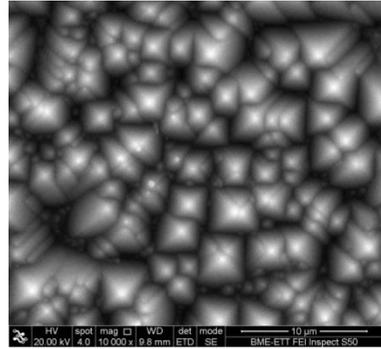
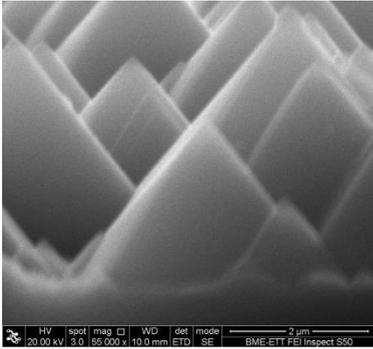
#### **4. New scientific results**

During my research, I worked out new processes and layer structures that can be utilized in the manufacturing technology of monocrystalline n-type silicon semitransparent solar cells. Based on these I realized novel semitransparent solar cell devices. The new scientific results are presented in 4 theses and 10 sub-theses.

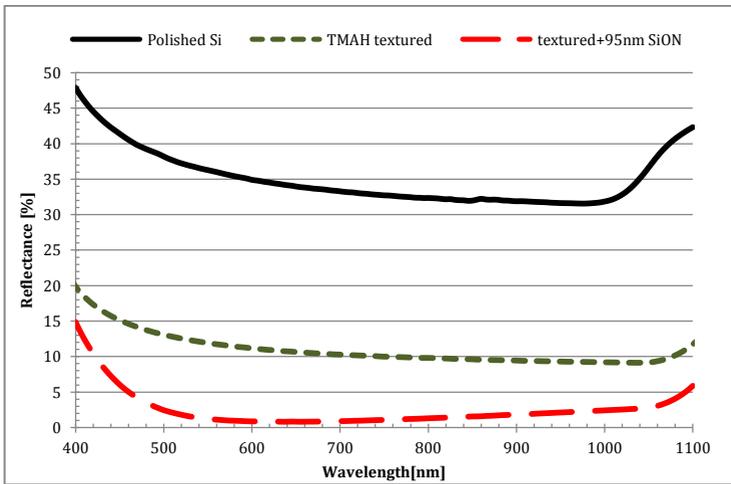
**Thesis 1.:** *I have elaborated a new technological process which can be applied for reducing the surface reflectance of n-type monocrystalline silicon wafer. The developed process can be integrated into the semitransparent solar cell technology. An average surface reflectance value of 2.5% can be obtained, this result is competitive with values of commercial solar cells (3.4-7.1%) [J2, C2, C4, C6].*

**Sub-thesis 1.1.:** *By utilizing a metal ion free etchant (2% TMAH and 6% IPA water solution) I obtained a homogeneous pyramidal structure on the silicon wafer surface. I have defined the etching parameters needed for a reproducible surface texturing process:  $T=80^{\circ}\text{C}$ ,  $t=30$  minutes. With the help of measurements, I have demonstrated that the surface pyramidal coverage is higher than 99%, and after the texturing process the average reflectance decreases to 11.28% in the 400-1100nm wavelength range. The height of the obtained pyramids is 1-4 $\mu\text{m}$ , which can have a positive influence on the quality of the lithographic process used in the semitransparent solar cell technology.*

**Sub-thesis 1.2.:** *I have further decreased the surface reflectance of structured monocrystalline silicon between 400-1100nm wavelengths to 2.5% by applying a single layer of RF sputtered silicon oxynitride ARC layer. The refractive index of the RF sputtered layer in argon and nitrogen atmosphere is 1.8893 ( $\lambda=587\text{nm}$ ). With the help of measurements, I demonstrated that the ARC layer reflectance curve can be changed by altering the nitrogen pressure.*



**Figure 1.:** SEM<sup>7</sup> image of the textured surface realized with etchant presented in sub-thesis 1.1. (used for determination of surface uniformity and pyramid size).



**Figure 2.:** Hemispherical reflectance curve of TMAH surface textured and ARC<sup>8</sup> layer coated surface, showing significant reflectance reduction relative to the polished surface.

<sup>7</sup> Scanning electron microscope

<sup>8</sup> Antireflection coating

**Thesis 2.:** *I have elaborated a technological process which can be employed for the formation of through silicon holes that have a rectangular cross-section. The technological process is based on TMAH wet anisotropic etching and can be used for semitransparent solar cell manufacturing purposes [J2, J3, C1, C4, C5, C6].*

**Sub-thesis 2.1.:** *For the realization of the through-holes, I optimized the anisotropic etchant composition and the technological parameters of the wet etching process in order to obtain the maximal etching rate. I have experimentally demonstrated that by using the optimized etchant at 92°C (5% TMAH solution and 2g/l/h ammonium persulphate), an average etching rate of 91µm/h with a depth deviation of less than 0.4% can be reached for an n-type, 5-10 Ωcm resistivity, <100> orientation silicon wafer.*

<b>TMAH concentration [wt.%]</b>	<b>Average etching rate [µm/h]</b>	<b>Standard deviation [%]</b>
3	81.2	4.9
<b>5</b>	<b>90.2</b>	<b>2.4</b>
7	83.5	1.3
<b>AP quantity [g/l/h]</b>	<b>Average etching rate [µm/h]</b>	<b>Standard deviation [%]</b>
<b>2</b>	<b>91.4</b>	<b>0.36</b>
3	88.4	0.46
5	86.9	0.49
8	85.1	0.89

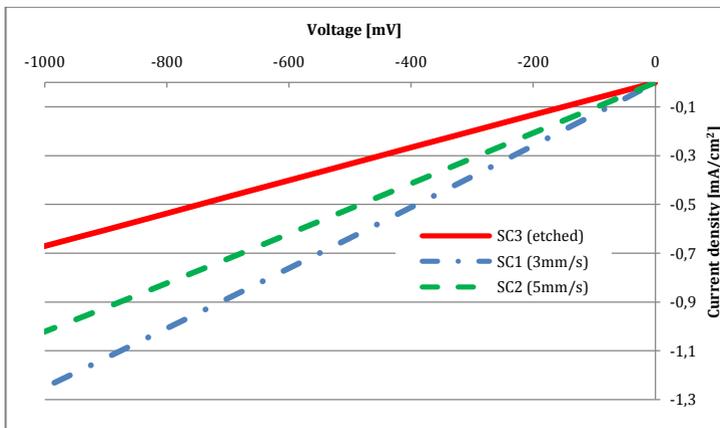
**Table 1.: Average Si etching rates in function of TMAH concentration and for different quantities of ammonium persulphate (in case of 5% TMAH concentration)**

**Sub-thesis 2.2.:** *I have demonstrated that for longer etching procedures the thermally grown silicon dioxide is the optimal masking layer – considering the material structure, the layer formation and the layer patterning – opposite to the silicon nitride that requires additional processes for the patterning, and the APCVD silicon dioxide that contains pinholes.*

**Sub-thesis 2.3.:** *I have experimentally proven that the dimension and density of the defects obtained after wet etching process decreased when the thermal annealing temperature of the single SOG (spin-on glass) layer was raised. SOG was considered as a low temperature (≤800°C) substitute masking layer during anisotropic etching procedures. After thermal annealing at 800°C the typical size of the inverted shapes and their groups decreased to 6µm or less. I do not recommend usage of SOG in the semitransparent solar cell technology.*

**Thesis 3.:** *I have demonstrated with help of test structures, that in case of anisotropic etching based technology no heat affected zone is present, contrary to laser cutting. The heat affected zone can lead to parasitic leakage or increased surface potential near the through-holes. Heat affected zone is characteristic for laser cutting, I have verified its presence in case of laser cut test structures. The structure of samples was identical to the one of the sample prepared with anisotropic etching technology. Anisotropic etching, as through-hole formation method, is advantageous for semitransparent solar cells; it can be utilized for realization of cells with favourable properties [4, C3].*

**Sub-thesis 3.1.:** *Based on the reverse bias characteristics I have confirmed that the shunt resistance of the samples varies in function of the through-hole forming method applied. The highest shunt resistance is in case of the semitransparent solar cell manufactured with anisotropic etching, the shunt resistance value decreases in the presence of a heat affected zone. In case of laser cut test cells, I have demonstrated that the shunt resistance value can drop to approximately half of the etched sample.*



**Figure 3.:** Reverse bias characteristic of laser cut and TMAH etched semitransparent solar cells (used for shunt resistance determination)

**Sub-thesis 3.2.:** *By analysing surface potential maps obtained with vibrating capacitor Kelvin method, I have proved that in the environment of the through-holes formed with anisotropic etching there is no potential band deviating from the substrate potential. I have demonstrated on test structures, that the amount of heat stress caused by laser cutting can influence the*

surface state density, leading to bands with altering width and potential near the through-holes.

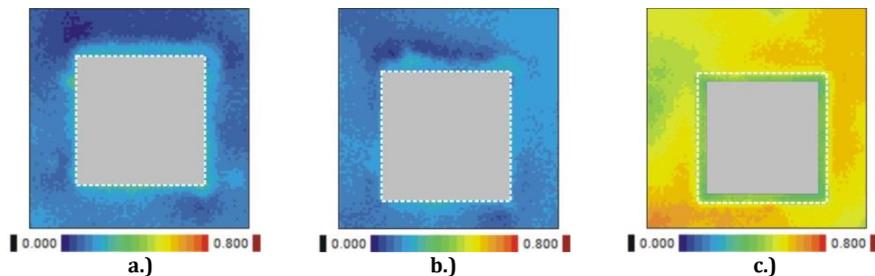


Figure 4.: Surface potential maps: a.) SC1(3mm/s), b.) SC2(5mm/s), c.) SC3(etched)

**Thesis 4.:** *I have worked out a new, complete technological sequence based on silicon technology which can be used for manufacturing semitransparent solar cells. Three novel semitransparent solar cells were realized, the desired transparency was reached with wet anisotropic etching. The transparency was provided by the through silicon holes, the size and density of the holes can be varied by changing the masking layer pattern [J1, J2, J3, C1, C6].*

**Sub-thesis 4.1.:** *I have developed a new technological process that combines the benefits of simultaneous diffusion, TMAH surface texturing, double sided anisotropic hole formation and silicon oxynitride ARC layer. The simultaneous diffusion lowers the time and number of the high temperature processes. The process time of the high temperature step needed for the masking layer growth was further decreased by usage of double sided anisotropic hole formation method. The efficiency of the semitransparent solar cell reaches 9.6%.*

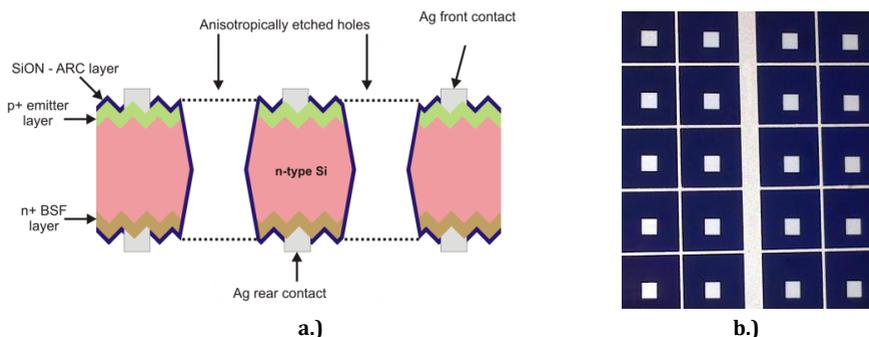


Figure 5.: Semitransparent solar cell: a.) cross-sectional view, b.) finished device

**Sub-thesis 4.2.:** Based on electrical measurements I confirmed that no difference can be found between the electrical parameters of identical technology based non-transparent and semitransparent solar cells, this way the formation of the through-holes has no additional parasitic effect. The technological process used for the through-hole formation does not influence the thermal behaviour of the completed devices.

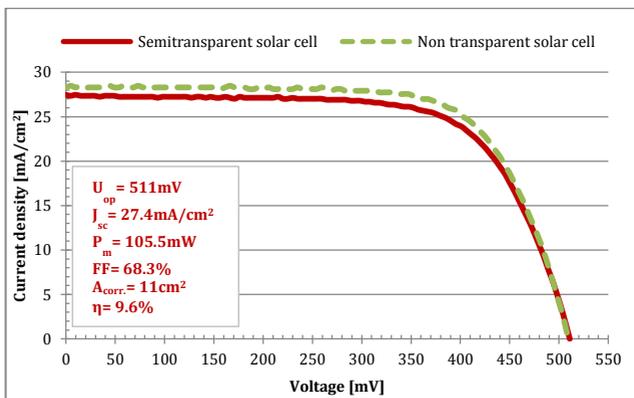


Figure 6.: J-V characteristics of semitransparent and non-transparent solar cells

**Sub-thesis 4.3.:** Based on measurements I have proved that the semitransparent solar cell structure presented in sub-thesis 4.1 is suitable for bifacially active operation. This is possible due to the incorporation into the device structure of the boron doped emitter, phosphorus doped back surface field, local metallization and rear antireflection coating.

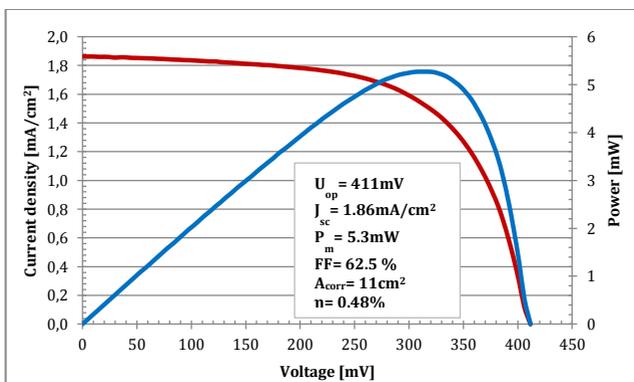


Figure 7.: J-V and P-V characteristics of the solar cell in case of rear illumination

## **5. Application of the results**

During my work I defined and elaborated layer processing methods and layer structures that can be used also in industrial environment, as standard or additional technological steps. The presented surface texturing and through silicon hole creation processes can also be used separately in solar cell or other silicon material based technologies. The research and development was done in the framework of the on-going K 100794 OTKA and finished PVMET projects, contributing to their achievements. The scientific paper containing the final experimental semitransparent solar cell structure and technology won the Best Paper Award at the 14<sup>th</sup> Biennial Baltic Electronics Conference in Tallinn. The accomplished novel semitransparent solar cell beyond integration possibilities into buildings can open up new perspectives even for smart systems where the transparent area of the solar cell can be used for a sensor placing surface. Besides the above mentioned exploitation of the results, the processes and structures can be further improved and the research work can be continued as part of new projects. The solar cell efficiency can be increased by utilization of higher minority carrier lifetime wafers.

## **Publications related to thesis points**

### **Journal papers**

[J1] B. Plesz, Á. Földváry, E. Báandy: *Low cost solar irradiation sensor and its thermal behaviour*, Microelectronics Journal, 42. volume, 5.issue, pp. 594-600, 2011

[J2] E. Báandy, M. Rencz: *Alternative technology used to manufacture semitransparent monocrystalline silicon solar cells*, Microsystem Technologies, 19. volume, 6. issue, pp. 819-827, 2013

[J3] E. Báandy, M. Rencz: *Thermal behaviour of new crystalline semitransparent solar cell structure*, Microelectronics Journal, 44. volume, 11. issue, pp. 1035-1043, 2013

[J4] E. Báandy, Á. Földváry, J. Mizsei: *Semitransparent monocrystalline solar cells manufactured by laser cutting and anisotropic etching*, Microsystem Technologies, 19. volume, 6. issue, pp. 837-844, 2013

### **Conference proceedings**

[C1] E. Báandy, M. Rencz: *Thermal characterisation of novel crystalline semitransparent solar cell*, Proceedings of the 17<sup>th</sup> International Workshop on THERMal INvestigation of ICs and Systems (THERMINIC'11), Paris, 2011, pp. 84-87

[C2] E. Báandy, Á. Földváry, V. Timár-Horváth: *Bifacially active n-type monocrystalline silicon solar cell*, Proceedings of the 6<sup>th</sup> International Workshop on Teaching Photovoltaics, Prague, 2012, pp. 70-73

[C3] E. Báandy, Á. Földváry, J. Mizsei: *Comparison of anisotropic etching and laser technologies applied in manufacturing of semitransparent monocrystalline solar cells*, Collection of Papers Presented at the Symposium on Design, Test, Integration and Packaging of MEMS/MOEMS (DTIP'12), Cannes, 2012, pp. 32-36

[C4] E. Báandy, M. Rencz: *New technology used to manufacture a simple semitransparent monocrystalline silicon solar cell*, Collection of Papers Presented at the Symposium on Design, Test, Integration and Packaging of MEMS/MOEMS (DTIP'12), Cannes, 2012, pp. 208-213

[C5] E. Báandy, Á. Földváry, M. Rencz: *The effect of heat treatment on spin-on oxide glasses in solar cell application*, Proceedings of the 19<sup>th</sup> International Workshop on THERMal INvestigation of ICs and Systems (THERMINIC'13), Berlin, 2013, pp. 297-300

[C6] E. Báandy, M. Rencz: *Enhanced semitransparent monocrystalline silicon solar cell structure*, Proceedings of the 14<sup>th</sup> Biennial Baltic Electronics Conference (BEC2014), Tallinn, pp. 29-32, Best Paper awarded publication

## **Additional publications**

[N1] E. Báandy, Á. Földváry, B. Plesz: *Thermal issues of solar irradiation sensor*, Proceedings of the 15<sup>th</sup> International Workshop on THERMal INvestigations of ICs and Systems (THERMINIC'09), Leuven, 2009, pp. 61-65

[N2] E. Báandy, Z. Pálffy, B. Plesz: *Spectral response measurement with modern LED light sources*, Proceedings of 5<sup>th</sup> International Workshop on Teaching Photovoltaics, Prague, 2010, pp. 63-68

[N3] E. Báandy, Á. Földváry, M. Rencz: *Thermally compensated intelligent irradiation sensor*, Collection of Papers Presented at the Symposium on Design, Test, Integration and Packaging of MEMS/MOEMS (DTIP'10), Seville, 2010, pp. 51-55

[N4] B. Plesz, E. Báandy, Á. Földváry, V. Timár-Hotvách, J. Mizsei: *Thermal behaviour of thin photoactive layer crystalline solar cells*, Collection of Papers Presented at the Symposium on Design, Test, Integration and Packaging of MEMS/MOEMS (DTIP'10), Seville, 2010, pp. 221-224

[N5] E. Báandy, Á. Földváry: *Intelligens fényintezitásmérő*, Műszaki Magazin, 6. volume, pp. 60-62