Schlussbericht

Zuwendungsempfänger:	Förderkennzeichen:
BTU Cottbus **Joint Lab IHP/BTU**	**03 SF 0352 C**

Vorhabenbezeichnung:

Verbundvorhaben:

Siliziumbasierte nanostrukturierte Dünnschichtmaterialien als innovative funktionale Elemente für hocheffiziente Solarzellen der nächsten Generation (SINOVA)

Teilvorhaben:

Lichtinduzierte Kristallisation und Charakterisierung von Si-Nanostrukturen

Laufzeit des Vorhabens:

01.03.2009 bis **29.02.2012**

Berichtszeitraum:

01.03.2009 bis **29.02.2012**

GEFÖRDERT VOM

Bundesministerium
für Bildung
und Forschung

im Rahmen der BMBF-Förderinitiative vom 09.07.2007
„Solar-Energie-Technik der nächsten Generation“,
BMBF-Förderprogramm
„Grundlagenforschung Energie2020+“

I. Kurzdarstellung

1. Aufgabenstellung

Ziel des Verbundprojekts war die Bearbeitung der technologischen Grundlagen zur Realisierung hocheffizienter Dünnschicht-Solarzellen auf Siliziumbasis. Im Fokus standen vor allem Konzepte, die das Shockley-Queisser-Limit für Si-Zellen mit „single junction“ von ca. 33% überschreiten. Hierfür sollte das Potential der Nanotechnologie mit seiner Technologieplattform zur funktionalen Verbesserung von Silizium-basierten Dünnschichtzellen gezielt eingesetzt und transferiert werden. Die Herausforderung für die Forschung im Materialsystem Silizium bestand darin, innovative funktionale Elemente zu schaffen, die die jeweiligen elektronischen und optischen Aufgaben in einer Solarzelle optimal erfüllen.

Die Arbeiten im BTU-Teilprojekt „Lichtinduzierte Kristallisation und Charakterisierung von Si-Nanostrukturen“ befassten sich schwerpunktmäßig mit der „Licht-induzierten Kristallisation“ und der „Optischen, elektrischen und photoelektrischen Charakterisierung“ der Absorber, die aus multiplen Si-Quantumwells (MQW) - eingebettet in dünne Isolatorschichten - bestanden. Die weitere Erforschung der lichtinduzierten Kristallisation (LIC) zielte ab auf das Erreichen einer hohen kristallinen Perfektion der Absorber-Schichten und auf ein verbessertes Verständnis der dem Kristallisationsprozeß zugrunde liegenden Mechanismen, um die angestrebten hohen Wirkungsgrade der MQW-Absorber erreichen zu können. Dabei war es wichtig, auch die dünnen a-Si-Schichten (< 5 nm) kristallisieren zu können, da sie auf Grund der großen effektiven Bandlücke besonders zur verlustarmen Nutzung des energiereichen Blauanteils des Sonnspektrums beitragen. Ein wesentlicher Schwerpunkt bei der Erforschung und Weiterentwicklung der lichtinduzierten Kristallisation bestand in der Erweiterung des Parameter-Raumes und der modellmäßigen Beschreibung des LIC-Prozesses.

Die „Optische, elektrische und photoelektrische Charakterisierung“ beinhaltete eine umfassende Charakterisierung der optischen und elektrischen Eigenschaften der kristallisierten Schichtstapel/Probenstrukturen. Die daraus gewonnenen Daten wurden dem vertieften Verständnis des LIC-Prozesses und zu einer Verbesserung und Optimierung der mit LIC verknüpften Herstellungs- und Kristallisationsprozesse genutzt.

2. Voraussetzungen, unter denen das Vorhaben durchgeführt wurde

Das Gemeinsame Labor des Instituts für innovative Mikroelektronik (IHP) Frankfurt (Oder) und der Brandenburgischen Technischen Universität (BTU) Cottbus - Joint Lab IHP/BTU in Cottbus -, das auf dem BTU-Campus in Cottbus angesiedelt ist, verfügt über langjährige Erfahrungen auf dem Gebiet der Si-Materialforschung, insbesondere zum Defect Engineering. Hauptarbeitsgebiete sind elektrische Aktivität von Kristalldefekten in Solar-Si, Si-Nanostrukturen, Versetzungs-Engineering für neuartige Bauelemente wie Lichtemitter und thermo-elektrische Generatoren auf Si-Basis und Si-Wafer für zukünftige Technologie-Generationen, dokumentiert in mehr als 200 Veröffentlichungen. Das Joint Lab betreibt Methoden der Halbleiter-Spektroskopie und -

Mikroskopie, die für das Projekt eingesetzt wurden, und ist darüber hinaus mit verschiedenen Lasern zur Materialbehandlung und einer UHV-Apparatur zur Pulsed-Laser-Deposition ausgestattet.
Die für die Erforschung des LIC-Prozesses an der BTU verwendeten Schichtstapel wurden vom Projektpartner IHT der RWTH Aachen bereitgestellt. Das IHT verfügt über langjährige Erfahrungen bei der Schichtabscheidung und konnte die erforderlichen Stapel aus amorphen Si-Schichten und Isolatorschichten (vorrangig Si-Oxid) mit Schichtdicken im nm-Bereich präparieren. Die erforderlichen strukturellen und analytischen Untersuchungen an den MQW wurden unter Einsatz elektronenmikroskopischer Verfahren von den Projektpartnern ER-C vom FZ Jülich und der RWTH Aachen sowie dem IZM der Martin-Luther-Universität Halle Wittenberg vorgenommen.
In die Bearbeitung der wissenschaftlichen Fragestellungen des Projektes an der BTU konnten erfahrene Wissenschaftler eingebunden werden. Ein Teil der Untersuchungen wurde von Doktoranden und Masterstudenten vorgenommen.

3. Planung und Ablauf des Vorhabens

Bereits in der Antragsphase wurden intensive Diskussionen zwischen allen Projektpartnern geführt, um die Inhalte und Ziele des SINOVA-Projektes abzustimmen. Daraus wurden die Aufgaben für alle Partner und die Meilensteine entwickelt. Diese durch offene, kritische und fordernde Diskussionen geprägte Zusammenarbeit wurde im Verlaufe des Projektes fortgesetzt und intensiviert. Dabei wurden regelmäßig mehrtägige Arbeitstreffen abgehalten, im Wechsel bei den verschiedenen Partnern des Verbundes. Auf diesen Treffen wurden neben der Analyse der erreichten Ergebnisse die Arbeiten für den nächsten Zeitraum detailliert abgesprochen. Daneben gab es zusätzlich intensive bilaterale Kontakte - einschließlich Proben- und Ergebnisaustausch - zwischen einzelnen Partnern. Die erzielten Ergebnisse wurden gemeinsam mit den jeweiligen Partnern publiziert.
Insgesamt wurden von uns die im Antrag vorgegebenen Zielsetzungen des Projektes erfüllt. Geringe Einschränkungen wurden in den BTU-Zwischenberichten für 2010 und 2011 angeführt (siehe auch Erfolgskontrollbericht).

4. Wissenschaftlicher und technischer Stand, an den angeknüpft wurde

Im Rahmen des 2008 abgeschlossenen BMBF-Projektes „Bandstrukturdesign: Ladungsträgertransport in Silizium-basierten Quantenstrukturen für zukünftige Höchstleistungs-Solarzellen“ wurden in Zusammenarbeit mit den Verbundpartnern, erste Ergebnisse erzielt, auf die unser Teilprojekt zum Teil aufbauen konnte. Dazu zählten beispielsweise die Beiträge zu Verspannungen in Si/Si-Oxid-Schichtstapeln, zu strukturellen und optischen Eigenschaften von Si/Si-Oxid-Schichtstapeln oder zur Laser-Kristallisation von dünnen Si-Schichten.
Zur Information über den bekannten Wissensstand wurde die gängige Fachliteratur genutzt, d.h. Zeitschriften wie Appl. Phys. A - Appl. Phys. Lett. - Appl. Surf. Sci. - J. Cryst. Growth - J. Appl. Phys. - J. Phys. Chem. B - J. Phys.: Condens. Matter - J. Vac. Sci. Technol. A - Mater. Sci. Eng. B - Nature - Phys. Rev. B - Phys. Rev. Lett. - Phys. Stat. Sol. - Science -

Semicond. Sci. Technol. - Superlattices Microstr. - Thin Solid Films und andere wurden ausgewertet. Natürlich wurden auch Konferenzbesuche, wie z.B. E-MRS, NANO 2010, BIAMS 2010, GADEST usw. zur Einholung von Informationen genutzt. Weiterhin wurde der Informationsdienst INSPEC herangezogen.

5. Zusammenarbeit mit anderen Stellen

Das Projekt wurde gemeinsam mit den Verbundpartnern Institut für Halbleitertechnologie (IHT) der RWTH Aachen, Abteilung Silizium-Photovoltaik (SEI) des Helmholtz-Zentrum Berlin, Institut für Energieforschung (IEF-5) des Forschungszentrums Jülich, Ernst Ruska Centrum (ER-C) des FZ Jülich und der RWTH Aachen, Interdisziplinäres Zentrum für Materialwissenschaften (IZM) der Martin-Luther-Universität Halle-Wittenberg sowie Institut für Festkörpertheorie und -optik (IFTO) der Friedrich-Schiller-Universität Jena durchgeführt. Entsprechend unserer Projektaufgaben und Ziele wurde besonders intensiv mit dem IHT, dem IZM und dem ER-C zusammen gearbeitet (vergl. auch oben, Pkt. 2), was auch die Autorenschaft in der Liste der Publikationen zum Ausdruck bringt.

II. Eingehende Darstellung

1. Verwendung der Zuwendung und des erzielten Ergebnisses im Einzelnen, mit Gegenüberstellung der vorgegebenen Ziele

Die von uns erzielten Resultate zum Teilvorhaben „Lichtinduzierte Kristallisation und Charakterisierung von Si-Nanostrukturen“ im Rahmen des BMBF-Verbundprojektes SINOVA sind ausführlich in der Anlage ‚Ergebnisse‘ (20 Seiten) in englischer Sprache dargestellt.

2. Wichtigste Positionen des zahlenmäßigen Nachweises

Nahezu die gesamte Summe der bewilligten Mittel wurde für unser Teilvorhaben benötigt und ausgegeben, d.h. 196.505 € (bewilligt 196.600 €). Auch die Ausgaben für die Einzelpositionen entsprechen fast den in der Bewilligung aufgeführten Teilsummen: Personalmittel 170.856 € (bewilligt 168.400 €), Sachmittel 17.695 € (19.050 €), Reisemittel 7.954 € (9.150 €). Zusätzliche Ausgaben wurden aus dem Haushalt bestritten.

3. Notwendigkeit und Angemessenheit der geleisteten Arbeit

Ausgehend von der BMBF-Förderinitiative „Solar-Energie-Technik der nächsten Generation“ im BMBF-Förderprogramm „Grundlagenforschung Energie2020+“ war es notwendig auszuloten, inwieweit Si-basierte nanostrukturierte Dünnschichtmaterialien als innovative Elemente für Solarzellen der nächsten Generation dienen können, d.h. grundlegend zu erforschen in welchem Ausmaß sie das ihnen theoretisch vorhergesagte Potential zur Steigerung des Wirkungsgrades gerecht werden. Es war angemessen, dieser Fragestellung im Rahmen des Verbundprojektes SINOVA nachzugehen, und dabei im BTU-Teilprojekt Absorber zu erforschen, die aus multiplen Si-Quantumwells (MQW) - eingebettet in dünne Isolatorschichten – bestehen. Insbesondere unter dem Aspekt

einer zukünftigen Applikation wurde ihre Realisierbarkeit unter Einsatz der lichtinduzierten Kristallisation und die erzielbare Qualität untersucht.

4. Voraussichtlicher Nutzen, insbesondere der Verwertbarkeit des Ergebnisses im Sinne des fortgeschriebenen Verwertungsplans

Die BTU Cottbus mit dem Joint Lab IHP/BTU und das IHP Frankfurt (Oder) haben durch die Arbeit am Projekt ihre Kompetenz im Bereich von Photovoltaikforschung, Si-Materialforschung und Diagnostik ausbauen können. Durch die Arbeit am Projekt konnte an der BTU das Interesse an der Thematik Photovoltaik verstärkt werden. In diesem Zusammenhang wurden Vorlesungen zur Photovoltaik angeboten, die gut angenommen wurden. Eine Masterarbeit mit unmittelbarem Projektbezug wurde erfolgreich abgeschlossen. Mit Vorträgen auf nationalen und internationalen Konferenzen und Publikationen in Fachzeitschriften wurden die Ergebnisse der wissenschaftlichen Öffentlichkeit vorgestellt und die wissenschaftliche Leistungsfähigkeit von BTU und IHP demonstriert.

Auf der Grundlage der erzielten Ergebnisse wird eingeschätzt, dass der im Projekt erreichte Verständnisgrad zur lichtinduzierten Kristallisation ausreicht, um im Bedarfsfall mit der Entwicklung einer Versuchsanlage beginnen zu können, mit der sich großflächige Absorber aus multiplen Si-Quantumwells (auf Quarzsubstrat) kristallisieren lassen.

Neben einer potentiellen Nutzung der lichtinduzierten Kristallisation für Absorber in Solarzellen der 3. Generation zeichnen sich aus unserer Sicht weitere Nutzungsmöglichkeiten dieser Technik ab:

- Wir haben gezeigt, dass sich auch dickere Si-Schichten (mehrere 10 nm) kristallisieren lassen. Diese ließen sich vermutlich als Keimschichten für die Dünnfilm-Si-PV auf Glas einsetzen.
- Die gewonnenen Erkenntnisse zur lichtinduzierten Kristallisation ließen sich wahrscheinlich auch nutzen, um leitfähige kristalline Nano-Strukturen/Schichten zu erzeugen, die eingebettet in Isolatoren (Si-Oxid), neuartige Materialien (hybride Si Schichten vom Typ „Electron crystal – Phonon glass“) für Si-basierte thermoelektrische Generatoren liefern könnten. Es gibt Überlegungen, diese Idee in einem noch zu beantragenden Vorhaben zu erforschen. Beteiligte aus dem SINOVA-Verbund könnten dabei sein das IHT Aachen, das IZM Halle und die BTU Cottbus.

5. Während der Durchführung des Vorhabens dem ZE bekannt gewordener Fortschritt auf dem Gebiet des Vorhabens bei anderen Stellen

Von anderen Stellen sind uns keine Fortschritte zur lichtinduzierten Kristallisation bekannt geworden, die über den im Rahmen des SINOVA-Projektes erreichten Stand hinausgehen.

6. Erfolgte oder geplante Veröffentlichungen des Ergebnisses nach BNBest-BMBF 98, Nr. 6

Publikationen (5 erschienen, 1 eingereicht)

[1] *“Light induced solid-phase crystallization of Si nanolayers in Si/SiO2 multiple quantum wells”,* T. Mchedlidze, T. Arguirov, S. Kouteva-Arguirova, and M. Kittler
JOURNAL OF APPLIED PHYSICS, Vol. 107, Article Number: 124302 (9 pages) (2010).
[2] *“Characterization of thin film photovoltaic material using photoluminescence and Raman spectroscopy”,* T. Mchedlidze, T. Arguirov, S. Kouteva-Arguirova, and M. Kittler, SOLID STATE PHENOMENA Vols. 156-158, 419 (2010).
[3] *“Scanning probe studies of amorphous silicon subjected to laser annealing”*, M. Ratzke, T. Mchedlidze, T. Arguirov, N. Acharya, M. Kittler, and J. Reif
PHYSICA STATUS SOLIDI (C), Volume 8, pp. 1351-1355 (2011).
[4] *“Structural characterization of crystallized Si thin film material by HRTEM and Raman spectroscopy”,* T. Mchedlidze, M. Beigmohamadi, B. Berghoff, R. Sohal, S. Suckow, T. Arguirov, N. Wilck, J. Mayer, B. Spangenberg, and M. Kittler
PHYSICA STATUS SOLIDI (A), Volume 208, pp. 588-591 (2011).
[5] *“Fast light-induced solid phase crystallization of nanometer thick silicon layers on quartz”*, T. Mchedlidze, T. Arguirov, and M. Kittler
SOLID STATE PHENOMENA, Vols. 178-179, pp. 110-115 (2011).
[6] *“Light induced crystallization of an amorphous silicon film embedded between silicone oxide layers”*, M. Schade, T. Mchedlidze, M. Kittler, and H. S. Leipner
THIN SOLID FILMS, submitted (September 2011), revised version in Begutachtung

Präsentationen (5 internationale und 2 nationale Konferenzen, 6 Projekttreffen)

[1] 13th International meeting on “Gettering and Defect Engineering in Semiconductors” (GADEST 2009), 26. Sept. - 2. Okt. 2009, Döllnsee-Schorfheide. Oral presentation:
“Characterization of thin film photovoltaic material using photoluminescence and Raman spectroscopy”.
[2] The E-MRS 2010 Spring Meeting, June 2010, Strasbourg, France. Oral presentation:
“Crystallization of thin Si layers by light: possible reasons for wavelength dependence”.
[3] 10th International Workshop on Beam Injection Assessment of Microstructures in semiconductors, (BIAMS 2010), July 2010, Halle (Saale). Oral presentation:
“Scanning probe studies of amorphous silicon subjected to laser annealing”.
[4] The X International Conference on “Nanostructured Materials” (NANO 2010), September 2010, Roma, Italy. Poster presentation:
“Fast solid phase crystallization of nanometer thick silicon layers by light”.
[5] Photovoltaic meeting, 24 Sept 2010, BTU, Cottbus. Oral presentation:
“Third generation PV cells based on Si/SiO_2 multiple quantum wells with nanometer thick Si layers”.
[6] SINOVA project meeting, 08 Mar 2010, Halle. Oral presentation:
"Mechanism of light-induced solid phase crystallization for Si thin-film materials".
[7] SINOVA project meeting, 21 Oct 2010, Aachen. Oral presentation:
"The wavelength dependence in light induced crystallization and AFM investigation of crystallized films".

[8] SINOVA project meeting, 25 Mar 2011, Jena. Oral presentation:
“Installation for fast light-induced solid phase crystallization process".
[9] 14th International meeting on “Gettering and Defect Engineering in Semiconductors”, GADEST 2011, September 2011, Loipersdorf, Austria. Oral presentation:
“Fast light-induced solid phase crystallization of nanometer thick silicon layers on quartz”.
[10] 48. Arbeitskreis Punktdefekte, 13-14 Oct 2011, Dresden. Oral presentation: *“Crystallization of silicon nano-layers by light”.*
[11] SINOVA project meeting, 18 Oct 2011, Cottbus. Oral presentation:
“Light-induced crystallization in SiC/$SiO_{1.2}$ MQW on glass".
[12] SINOVA project meeting, 18 Oct 2011, Cottbus. Oral presentation:
“Influence of a substrate on LISPC process”.
[13] SINOVA project meeting, 23 Febr 2012, Aachen. Oral presentation:
“Influence of hydrogen content and external conditions on light-induced crystallization in Si/SiO_2 MQW on glass “.

Anlagen

- Ergebnisse
- Erfolgskontrollbericht
- Berichtsblatt und Document Control Sheet

Anlage zu Pkt. 2 des Schlussberichtes

Ergebnisse

Teilvorhaben

Lichtinduzierte Kristallisation und Charakterisierung von Si-Nanostrukturen

Förderkennzeichen

03 SF 0352 C

als Bestandteil des BMBF-Verbundprojektes

Siliziumbasierte nanostrukturierte Dünnschichtmaterialien als innovative funktionale Elemente für hocheffiziente Solarzellen der nächsten Generation

SINOVA

gefördert im Rahmen der BMBF-Förderinitiative „Solar-Energie-Technik der nächsten Generation“
BMBF Förderprogramm „Grundlagenforschung Energie2020+“

Laufzeit

01.03.2009 - 29.02.2012

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According to the program of "SINOVA" project, our investigations were concentrated in three directions: (1) Development and perfection of characterization methods for the nanometer size Si crystalline films, multi-quantum wells and dots (AP 4); (2) Further development and optimization of light-induced crystallization, fundamental aspects (AP 3.1); (3) Development of technique and investigation of conditions for practical application of light-induced crystallization (AP 3).
Below we will present the key results obtained in these three directions.

AP 4. (a) Structural characterization of crystallized Si thin film material by HRTEM and Raman spectroscopy.

Substantial improvement and reliable control of the crystalline quality of thin Si films and Si nano-layers in Si/SiO_2 MQWs remains a priority task, since only high degree of crystallinity can lead to suitable electrical and PV characteristics of the films. Transmission electron microscopy (TEM) and Raman spectroscopy (RS) are well applicable for the structural investigations of nanometer size crystalline Si objects. However, each of these methods has its advantages and drawbacks. It was necessary to compare directly RS and TEM results for the same sample for correlation of the information provided by the methods. We decided to perform a direct comparison of RS and TEM results for the relatively simple case of a single 60 nm thick Si layer, deposited on fused quartz between two SiO_2 layers. Sample was subjected to crystallization in furnace at 1050ºC during 30 min.

Comparison of the HRTEM and RS results.

▪ Both experimental methods applied for structural characterization showed high degree of crystallization of the thin crystallized Si film. HRTEM images show presence of crystalline grains filling the volume of the film almost entirely, while RS results suggest high value of crystalline fraction, i.e. $F_{CR}\approx 74\%$. The high level of crystallinity visible in the HRTEM images does not exclude presence of a-Si inclusions in the material of the film, obscured by the crystalline material.

▪ Possible errors in estimations of F_{CR} value by RS are related to the origin and spectral intensity of 488 cm^{-1} peak. The peak at ~480 cm^{-1} can originate from grain boundaries (GB) or stishovit, a variety of SiO_X (X<2). Since diffusion of Si atoms to the neighbouring oxide and formation of SiO_X phase there during furnace annealing of the sample can not be excluded, the peak at ~480 cm^{-1} can contain a component related to SiO_X. In such a case the estimation of F_{CR} from the RS results would be understated. Altogether, we can state a good agreement between HRTEM and RS results in analysing the crystallinity of the material.

▪ From the first glance there exists disagreement between sizes of Si-nc grains obtained from HRTEM and RS results, i.e. the RS gives s_{nc}~4.2 nm for the average grain size, while large grains with s_{nc}>20 nm could be found in HRTEM images. However, one should keep in mind that RS suggests a mean value for the size of the grains. The asymmetric shape of the Si-nc peak indicates a large scatter of the actual grain sizes. On the other hand observation of small size grains (<3 nm) in HRTEM is problematic due to concealing of their images by the large grains. Taking into consideration the above details, the agreement between the HRTEM and RS results in analysing of Si-nc dimensions can be recognised as quite satisfactory.

▪ ***Summarizing***, results obtained by HRTEM and by RS during investigations of structural parameters of 60 nm thick crystallized Si film showed nice agreement. Both methods showed that the film contains high density of Si-nc grains with mean size about 4 nm (RS) and a large scatter of individual sizes (from s_{nc}<3 nm to s_{nc}~20 nm, HRTEM). The fraction of crystalline material in the film exceeds 74%. HRTEM results suggest large scatter in orientations of the Si-nc grains and presence of boundary defects between the neighbouring grains. RS revealed high average compressive strain (~4.8 GPa) in the system and the presence of the high pressure Si-III and Si-XII phases in the material of the crystallized film.

The results of this investigation were published in the journal:

T. Mchedlidze, M. Beigmohamadi, B. Berghoff, R. Sohal, S. Suckow, T. Arguirov, N. Wilck, J. Mayer, B. Spangenberg, and M. Kittler, "Structural characterization of crystallized Si thin film material by HRTEM and Raman spectroscopy", PHYSICA STATUS SOLIDI (A) Volume 208, pp. 588-591 (2011).

AP 4. (b) Scanning probe studies of thin amorphous silicon film subjected to LISPC.

▪ In order to investigate the changes in the morphological structure of the LISPC subjected samples, AFM using platinum covered tips was applied ("Smena" microscope by NTMDT). The starting samples contained 60 nm a-Si film, deposited on quartz substrate with thin (5 nm) intermediate layer of SiO_2. On the top of the film 110 nm thick SiO_2 cover layer was deposited. After LISPC at various P_{LAS}, the crystalline structure of the samples was evaluated by Raman spectroscopy (RS) and the crystalline fraction was estimated for the samples.

▪ In addition to the AFM mapping of the surface topography using the Semi-contact Mode, the Phase lags between the applied driving force and the registered oscillation of the AFM tip was simultaneously recorded allowing estimations on the elastic properties of the sample. Further, in

order to check more thoroughly the surface itself, the lateral force acting on the tip during a Contact Mode scan was measured, yielding information on friction. The combination of these three methods gives the opportunity to decide if apparent changes to the local topography were triggered by processes at the surface or beneath.

▪ For the sample area exposed to near-to-optimal laser intensity, shrinkage of the thickness of the layers can be observed as illustrated in Fig. 1. The topography (a) of this spot is characterized by a very smooth but impressed inner region and the outer region which is thicker than the initial structure. The shrinkage of the inner part well corresponds to the LISPC process, where the thickness is reduced due to the higher density of the crystallized material. The increase of the thickness at the borders of the illuminated area should be attributed to oxidation of the material and the related expansion of the layer. The reason for the oxidation may be related to additional time for the heating of the structure at the border locations due to stopping of the scan process there.

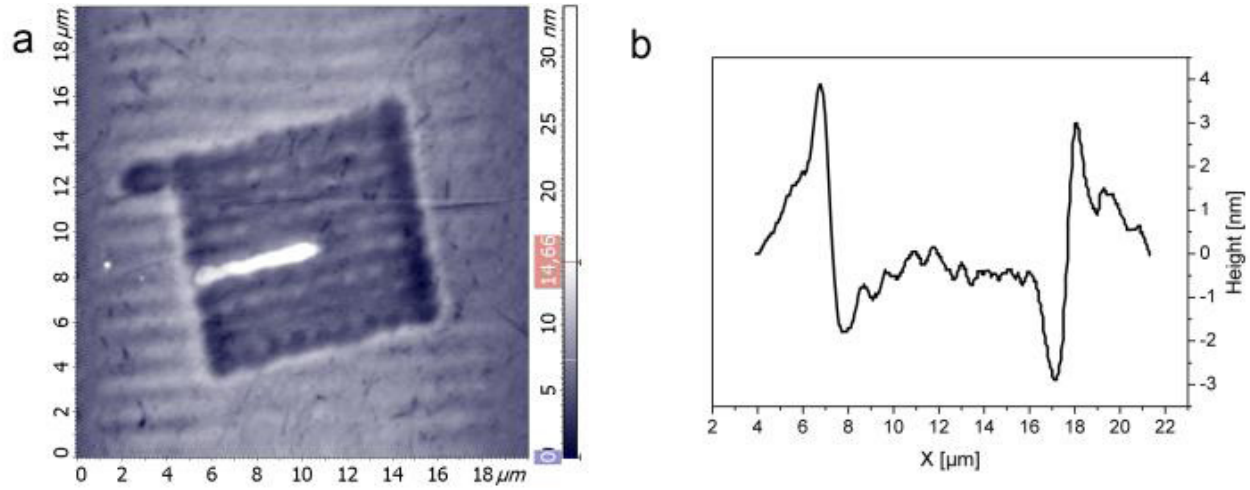


Fig. 1. *AFM topography image (a) and average height profile (b) from an area irradiated with close to optimal laser power. Clearly, there is a shrinking of the material, deducible from the impression of the inner region by about 1 nm, and some secondary impact on the outer region suggested by the growth by about 2 nm.*

▪ It is evident by comparing the Tapping Mode Phase map and the Contact Mode Lateral Force map taken from the same area that the reported change in sample surface is not due to material removal by evaporation. The expected difference in elastic properties between crystalline and amorphous silicon will create a reasonable difference in the effective Young's modulus and thus in the detected phase signal.

▪ If one compares the apparent heights of the irradiated areas for different applied laser intensities, two regions of interaction can be distinguished (see Fig. 2). For low laser powers, the surface is impressed by an amount which is increasing along with power. The maximum change in depth found

was ~ 10 nm. For higher intensities, a huge increase of surface height up to about 60 nm was recorded. Interestingly, the threshold for this expansion is close to the optimum laser power.

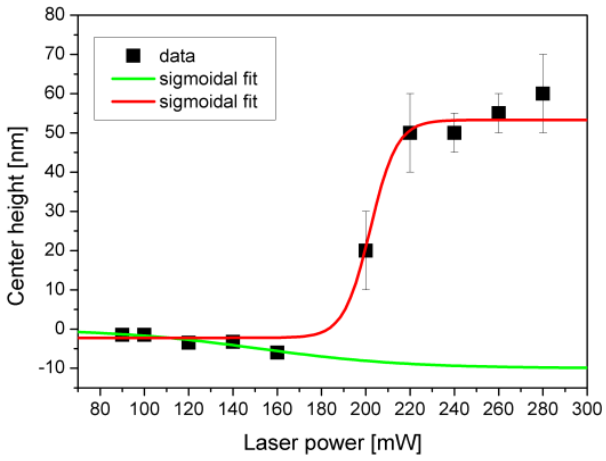


Fig. 2. *Evolution of the surface height. There are two apparent regions attributed to different processes: A shrinking due to crystallization for lower powers and an expansion because of oxidation at higher powers. Note that the laser power on the sample is about one tenth of the values reported in the graph.*

▪ The observed behavior can be readily explained by either crystallization, causing a densification of the silicon expressed here as shrinking by small amounts, or formation of silicon oxide phases known to increase the thickness of the film due to the difference in density by a factor of two. This interpretation is depicted using sketch in Fig. 3, assigning the surface profile to the grade of crystallization and oxidation. In this model, the oxidation starts from some residual amorphous layers surrounding the still-growing crystalline core generating a range of powers with increasing surface height and increasing Raman signal strength (between points 0.8 and 1 of P_{LAS} in the sketch).

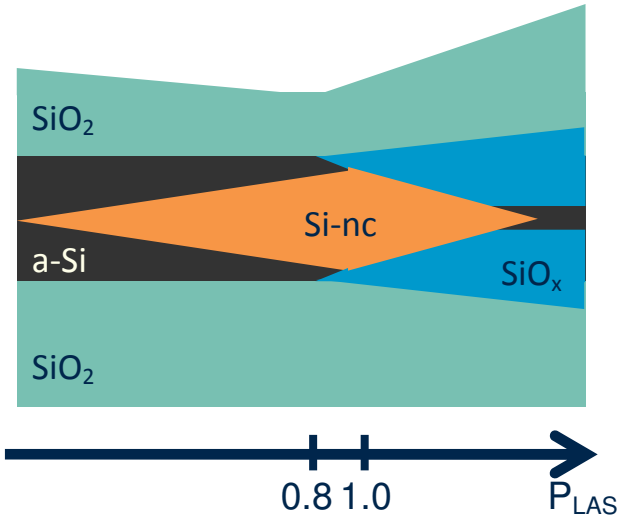


Fig. 3. *Model explaining the evolution of surface height and intensity of the c-Si Raman signal. The crystallization causes both shrinking and increase in Raman signal, while the oxidation explains expansion and decrease in signal. The optimal LISPC process proceeds between 0.8-1 of the* P_{LAS}.

▪ The results obtained from various scanning probe based investigations of light-crystallized amorphous silicon show, that the phase change can be detected by these methods by either measuring the height change or by mapping the phase shift in a Tapping Mode setup. A comparison

of SPM results with those obtained from Raman spectroscopy reveals that an oxidation of the silicon takes place even prior it could be detected by a decrease in Raman signal intensity.

▪ ***Summarizing,*** scanning probe measurement results supported the model of light-induced solid phase crystallization developed on the basis of Raman investigations. Both characterization methods show well comparable results.

The results of this investigation were published in the journal:

M. Ratzke, T. Mchedlidze, T. Arguirov, N. Acharya, M. Kittler and J. Reif, "Scanning probe studies of amorphous silicon subjected to laser annealing", PHYSICA STATUS SOLIDI (C) Volume 8, pp. 1351-1355 (2011).

AP 3.1 (a) Further development and optimization of light-induced crystallization, fundamental aspects: principles and model of LISPC process.

▪ For the detailed investigation of the LISPC process, interaction of the light radiation from the laser source at wavelength 532 nm with MQW was performed. The MQW initially contained six layers of amorphous silicon (a-Si) with thickness of d =10 nm, which were separated by 3 nm thick layers of silicon oxide (SiO_2). The layers were deposited on a quartz plate (see sketch in inset in Fig. 4).

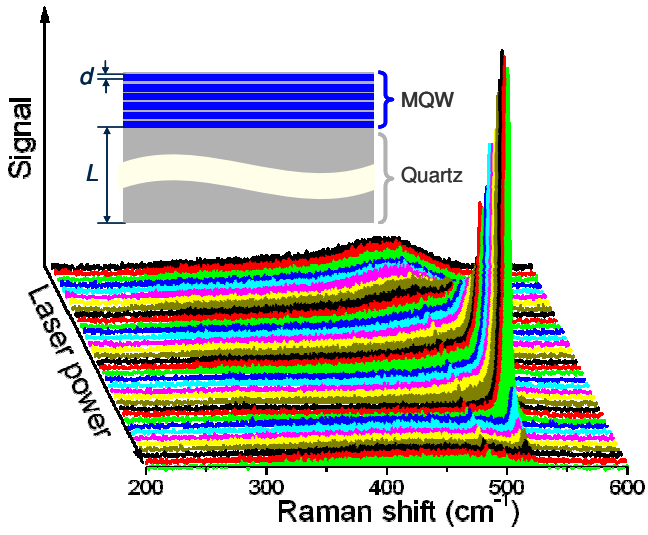


Fig. 4. *Change of the Raman spectra with the increase of the light flux during the treatments. The spectra gradually changes from fully a-Si at smallest power to fully crystalline and back, to amorphous-like shape. Inset shows structure of the MQW, blu layers correspond to Si, gray – to SiO_2, L≈1 mm.*

▪ Fresh areas 20×20 μm^2 in size were subjected to the radiation at various light fluxes. For this the beam from the laser focused to the diameter of 1 μm was scanned across a fresh area of MQW with the speed of 0.5 μm/sec. The power of the radiation at the surface of the sample was varied from 4 to 60 mW.

▪ The structure of the material in the light-treated areas was investigated using Raman spectroscopy. All Raman spectra, recorded from the sample are presented in Fig. 4. Details of several characteristic spectra are presented in Fig. 5.

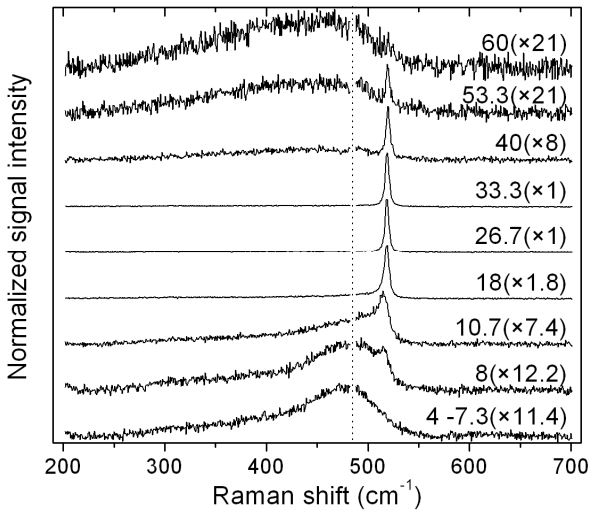


Fig. 5. *Evolution of Raman spectra for the MQW with variation of laser power, P_{LAS} at λ_{LAS}=532 nm. The spectra are shifted on vertical axis for clarity of presentation. The values of P_{LAS} in mW units and the magnification coefficients for the signal amplitude (in brackets) are indicated in the figure above each spectrum. Dotted line shows position of marker peak (Hg) used for precise calibration of wavenumbers.*

▪ Each Raman spectra was fitted with the separate peaks corresponding to a-Si, Si-clusters (Si-cl) and nanocrystalline-Si (Si-nc). The parameters of the peaks, i.e. intensity, peak maximum position and full-width on half maximum (FWHM) were used for characterization of the material in MQW and properties of Si-nc.

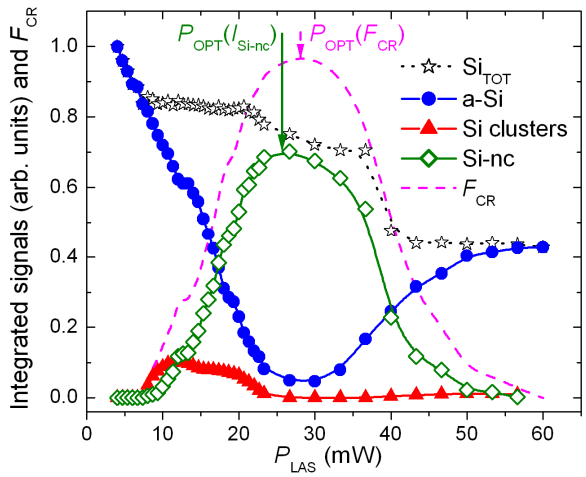


Fig. 6. *Dependence of integrated intensities of Raman peaks from various Si phases on P_{LAS} at λ_{LAS}=532 nm for the MQW. A cumulative signal from all Si-related phases is presented by Si_{TOT} and F_{CR} presents a fraction of Si-nc signal, i.e. $I_{Si\text{-}nc}/I_{SiTOT}$. Attribution of symbols is indicated in the figure. Curves are shown to guide the eye. Note a difference between optimal laser power values for maximal $I_{Si\text{-}nc}$ signal, $P_{OPT}(I_{Si\text{-}nc})$ and for maximal Si-nc fraction, $P_{OPT}(F_{CR})$.*

▪ Changes in the intensities of the Raman signals corresponding to various Si phases, i.e. a-Si, Si-cl and Si-nc, and to cumulative Si-related signal (Si_{TOT}) are presented in Fig. 6. In the same figure a variation of Si-nc fraction, i.e. of $F_{CR}=(I_{SI\text{-}nc}/I_{SiTOT})$ is presented. The figure clearly shows that there exists optimal light power for obtaining maximal Si-nc signal, i.e. $P_{OPT}(I_{Si\text{-}nc})$ and that optimal for obtaining $F_{CR}\approx1$, i.e. $P_{OPT}(F_{CR})$, and that for λ_{LAS}=532 nm $P_{OPT}(I_{Si\text{-}nc}) \neq P_{OPT}(F_{CR})$.

▪ Applying the previously established procedure, an average size of Si-nc, s_{nc} and a strain in the MQW, ε_{MQW} were estimated for each light flux value.

▪ Analyses of the results presented in Fig. 6 and data for size of nano-crystallites and the residual strain allows proposing several regimes for interaction of light with the MQW material. Namely:

- 4-7 mW: formation of "proto" – clusters, size < 1nm.
- 7-13 mW: preferential formation of Si clusters (size < 2nm, peak at 507cm-1).
- 13-23 mW: preferential formation of Si-nc. Increase of average Si-nc size from 4 to 10 nm.
- 23-30 mW: the optimal LIC conditions, average Si-nc size from 10 to 12 nm, i.e. Si-nc "fills" the layer.
- 30-40 mW: start of partial melting in the system, increase of compressive stress, a-Si again appears after the treatment.
- 40-55 mW: melting and dissolution of Si; clusters and a-Si detected. Compressive stress increases.
- >55 mW: Total volume of Si drops to detection limit, no Si-nc in the spectra.

▪ It should be noted that some polymorphs of stishovit, a variety of silicon oxide, SiO_X, (X<2), also exhibit Raman spectra similar to that of a-Si. Therefore, the spectra obtained after large P_{LAS} at least partly could be attributed to such oxide polymorphs. The last supposition was verified in experiments with subsequent laser annealing of MQWs already subjected to large P_{LAS}. For such MQWs it was impossible to select optimal P_{LAS} for complete crystallization, i.e. for achieving $F_{CR}\approx 1$.

▪ Starting from $P_{LAS}\approx 25$ mW average dimensions of Si-nc inclusions exceed thickness of the deposited a-Si layers. The condition $s_{nc}>d$, where d is the thickness of deposited a-Si layers, does not necessarily mean that Si layer thickness in MQW was changed; we suppose that this indicated on lateral growth of Si-nc phase inside the Si layers. On the other hand, it is necessary to note that FWHM value for the Si-nc peak for $s_{nc}\geq 14$ nm approaches that for c-Si peak in bulk material. Therefore, after $P_{LAS}\approx 40$ mW the value of s_{nc} does not necessarily correspond to the real dimensions of Si-nc inclusions.

▪ An efficiency of crystallization, η could be estimated from an expression:

$$\eta(\lambda_{LAS}) \propto \frac{I_{Si-nc}(\max)}{P_{OPT}\cdot[1-\exp(-\alpha d)]}\ , \qquad (1)$$

where the right side is proportional to a volume of crystallized material per absorbed power. The alternate measure of the efficiency can be the ratio between P_{OPT} ($I_{Si\text{-}nc}$) to P_{OPT} (F_{CR}), where the first presents optimal power for maximal Si-nc signal, while the second is the optimal power for the maximal crystalline fraction. Indeed, if all a-Si would be converted to Si-nc, both power values should coincide. If dissolution of Si atoms was significant, then obviously we would get P_{OPT} ($I_{Si\text{-}nc}$) < P_{OPT} (F_{CR}). From our investigations of LISPC at various laser wavelengths it was obtained that dependencies of the efficiencies on the laser wavelength have the maxima at the same wavelength value at ~ 490 nm. On the other hand, the maximum of the ratio of transmittances $T_0(\lambda)/T_{LIC}(\lambda)$ and

therefore maximum for $AR = \alpha_{a\text{-}Si}/\alpha_{Si\text{-}nc}$ measured for the MQW after LIC was observed between 490 nm and 500 nm. Similarity of the dependences suggests that preferential light absorption in a-Si may be the origin of the observed wavelength dependencies. Probably, at the wavelengths, which are different from the optimal value, λ_{OPT}, part of the absorbed energy is deflected on out-diffusion of Si atoms to the neighbouring SiO_2 and to formation of SiO_X (X<2) there.

• Kinetics of heating of the MQW material was calculated based on assumptions that the light is absorbed only in Si layers of MQW and heat transfer is determined by thermal properties of the substrate, i.e. quartz. This assumptions could be well justified since the absorption coefficient of quartz is very small at 532 nm and the small thickness of Si layers excludes their large influence on the heat transfer in the system. In the frame of the assumptions the heating of the MQW could be estimated using the existing expressions for heating of semi-infinite metal slabs by light based on the theory of Bartholomeus (see [B. J. Bartholomeusz, J. Appl. Phys., 73, 1066 (1993)]). These suppositions allowed us to propose an expression for the temperature increase in the structure with time under illumination:

$$\Delta T(\tau) = \frac{\alpha P_{ACT} \beta^2 \kappa (1-R)}{\pi k} \int_0^{\tau} \frac{\exp(\alpha^2 \kappa t)\operatorname{erfc}(\alpha\sqrt{\kappa t})}{1+4\beta^2 \kappa t} dt \qquad (2)$$

where α is absorption coefficient, P_{ACT} is power absorbed by the MQW, k is thermal conductivity, κ is thermal diffusivity, R is reflectance, $\beta = 1/\sigma_{eff}\sqrt{2}$, with σ_{eff} an irradiance radius of the laser spot. In this expression α, R and P_{ACT} are determined by the MQW film, while k and κ are parameters of the substrate. All parameters could be found in publications and from the experiment. In Eq.(2) the values shown in green characterize optical properties of the MQW film, while those shown in red characterize thermal properties of the substrate.

▪ The result of calculations for eq. (2) at λ_{LAS}=532 nm and starting temperature 290K are presented in Fig. 7. Blue dashed curve presents temperature change of MQW with a-Si layers, while brown dashed curve presents same for MQW with crystalline Si layers. If in MQW with a-Si layers crystallization starts at some temperature (shown by arrow in Fig. 7), the light absorption in the layer decreases and the temperature will follow the curve similar to that shown in Fig. 7 in violet colour.

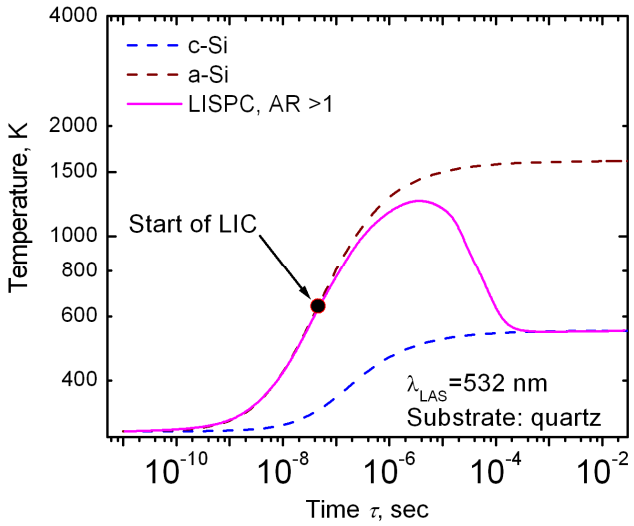


Fig.7. *Time dependence of the temperature of the sample surface under laser irradiation for a-Si and c-Si MQW on quartz estimated using eq. (2). Laser power corresponds to P_{OPT}. Attributions of the lines are presented in the figure.*

▪ Since the main reason of the difference in the heating is the difference in light absorption in the Si layers, the ratio of the absorption coefficients $AR=\alpha_{a\text{-}Si}/\alpha_{Si\text{-}nc}$ determines the process flow. Namely for $AR>1$ the process is self-regulated, with "negative feedback" from crystallization process, while for $AR\leq 1$ the process is uncontrollable. In the last case the process of crystallization is either very slow or proceeds through Si melting causing large stresses and incomplete crystallization in the layers.

▪ The obtained value $\lambda_{LAS} \approx 500$ nm for the optimal wavelength for LISPC corresponds to the maximal *AR* value, thus suggesting maximal difference in the heating between a-Si and Si-nc.

▪ ***Summarizing,*** LISPC process at optimal illumination conditions implies solid-to-solid transformation of a-Si to Si-nc due to absorption of light in a-Si film. The process is self regulated due to decrease of light absorption in MQW film after crystallization at optimal light wavelengths. Maximal efficiency of the process is achieved when the light energy is maximally applied for crystallization.

The results of this investigation were published in the journal:

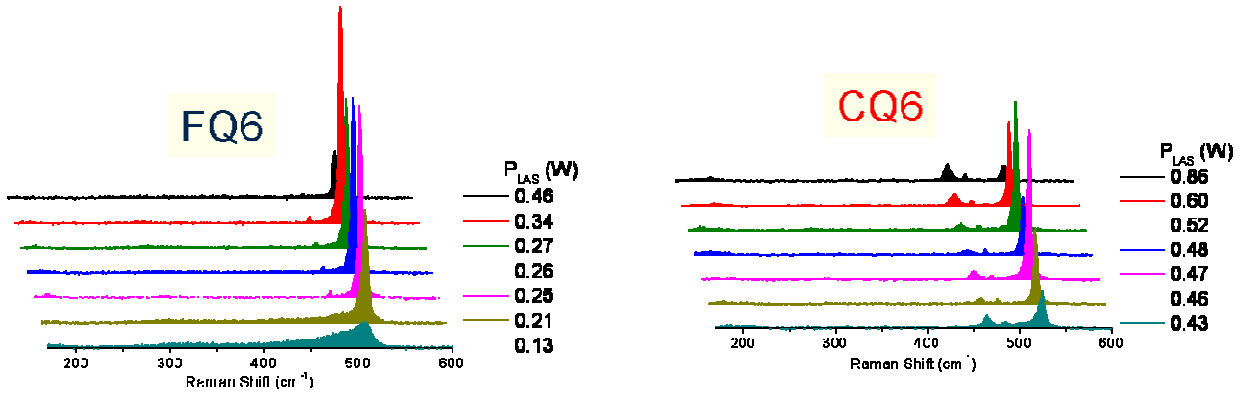
T. Mchedlidze, T. Arguirov, S. Kouteva-Arguirova, and M. Kittler, "Light induced solid-phase crystallization of Si nanolayers in Si/SiO_2 multiple quantum wells", JOURNAL OF APPLIED PHYSICS Volume: 107, Article Number: 124302 (9 pages) (2010).

AP 3.1 (b) Further development and optimization of light-induced crystallization, fundamental aspects: influence of substrate material.

▪ The model of LISPC based on eq. (2) implies strong influence of thermal properties of substrate material on the process. Our preliminary experiments with sapphire substrate also showed quite low efficiency of the LISPC process for that substrate. Special investigation was performed to determine influence of the substrate on LISPC and to find the optimal substrate material.

▪ Two substrates with similar optical properties but heaving different thermal parameters were chosen for the investigation. The first was fused quartz (fused silica, glass) and the second was crystalline quartz (α-quartz). Temperature dependencies for k and κ of these materials were obtained from the literature (see [H. Kinamori, J. Geophys. Res., **73,** 595 (1968)]). Both these substrates were used for RPECVD deposition of Si/SiO_2 MWQ with 6 pairs of 10 nm thick a-Si layers and 3 nm thick SiO_2 layers (MQW: 6 × (10nm Si + 3 nm SiO_2)) at 250ºC. The samples will be labeled as CQ6 for the sample with crystalline quartz substrate and FQ6 for the sample with fused silica substrate. The attribution of the substrate material was confirmed by separate Raman analyses.

▪ Light-induced crystallization of the samples was performed using the installation for fast light-induced crystallization (see part AP 3 (a) below). Areas of 0.5 mm^2 on the samples were crystallized using various power values of the cw laser (P_{LAS}) with the wavelength of 532 nm. Several resulting spectra detected from the laser treated areas of the samples are presented in Fig. 3. The figure shows that the a-Si material of the MQW layers transforms from the fully amorphous Si to Si-nc, with various intensities of Si-nc peak and finally Si-nc signal strongly decreases in the intensity upon increase of P_{LAS}.



(a) **(b)**

Fig.8. *Raman spectra detected from FQ6 (a) and CQ6 (b) MQW samples after light-induced crystallization at various values of laser power. The vertical scale of the graphs is the same. The values of the applied P_{LAS} are indicated to the left from the curves.*

▪ The optimal conditions for the LISPC was obtained at P_{LAS} =250 mW for the case of FQ6 sample and at P_{LAS} =470 mW for the CQ6 sample. Considering the light spot size on the sample surface these values correspond to fluxes 0.49 MW/cm^2 for FQ6 and 0.91 MW/cm^2 for CQ6 samples respectively.

▪ Analyses of the exact spectral positions of the Si-nc Raman peaks and their FWHM (full-width on half maximum) suggest larger crystallite sizes and tensile stress in FQ6 sample and smaller crystallite sizes and strong compressive stress in CQ6 sample after crystallization in optimal LISPC conditions. Structural results at optimal LISPC conditions for both structures are presented in Table I. Tensile residual stress in FQ6 sample corresponds to shrinkage of the Si layers after crystallization due to larger density of Si-nc in comparison to a-Si. However, compressive stress in CQ6 indicates on simultaneous oxidation of significant volume of Si, because oxide with smaller density generates compressive strain in the structure.

Table I. Optimal values of P_{LAS}, relative intensity of Si-nc peaks and structural parameters of the MQW samples after optimal crystallization conditions.

Sample	Optimal P_{LAS} (W)	Relative intensity of Si-nc peak	Si-nc size (nm)	Residual stress (GPa)
CQ6	0.47	1	9-10	+2.2 (compressive)
FQ6	0.25	1.3	10-11	-1.4 (tensile)

▪ Efficiencies of LISPC for the two investigated samples could be compared from the ratio of the coefficients estimated from eq. (1). Such a comparison suggests that for MQW on fused silica substrate the LISPC process is ~2.5 times more efficient than for MQW on crystalline quartz substrate (see Table I).

▪ To determine the reason for the worse performance of MQW on crystalline quartz substrate we performed modeling of the temperature changes in the samples under illumination using eq. (2). The results of the calculations are presented in Fig. 9. As seen from the figure, the final temperature and the rate of temperature increase are much larger in the case of CQ6 structure. In the frame of the developed LISPC model (see part AP 3.1 (a) above) these findings suggest that the structure passes the critical crystallization temperature (~1000 K) very fast, therefore the mechanism of self-regulation would be suppressed and Si will be partially melted. Crystallization from the melt will cause oxidation and large compressive strain in the resulting structure.

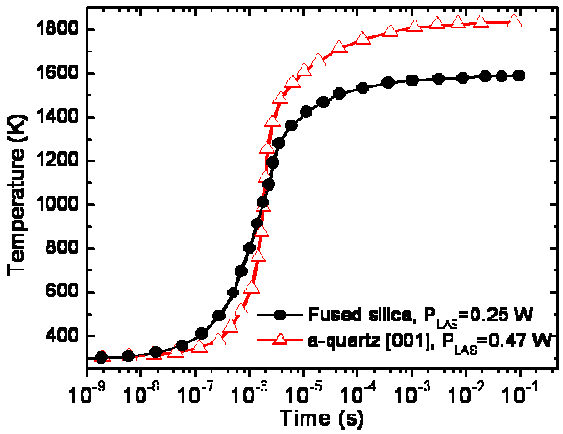


Fig.9. *Time dependences of the temperature of the sample surface under laser irradiation for the MQW on fused silica (black symbols and curve) and on crystalline quartz (red symbols and curve) substrates.*

▪ ***Summarizing***, substrate of the MQW film has strong influence on the LISPC process. The results obtained for samples on different substrates well fit the proposed mechanism for LISPC. The proposed model could be used for estimation of optimal LISPC conditions (e.g. optimal P_{LAS}) for the case of various substrates. Obviously, the substrate with lower thermal conductivity/diffusivity gives much better efficiency for the LISPC. From the substrates investigated until now, the fused silica looks optimal for LISPC.

AP 3.1 (c) Further development and optimization of light-induced crystallization, fundamental aspects: influence of dissolved hydrogen on LISPC of Si/SiO_2 MQW on glass.

▪ Large volume of hydrogen atoms are introduced to the Si/SiO_2 MQW layers during RPECVD process. The origin of hydrogen is the silane gas (SiH_4) used for a-Si deposition and the content of H atoms in the deposited material could reach tenths of percents depending on the deposition temperature (T_{dep}, see e.g. [N. Budini, et al., Thin Solid films 518, 5349 (2010)]). For the conditions used for deposition of the samples in our case, i.e. T_{dep}=250ºC, the amount of hydrogen is in the range 6-10%. Hydrogen in such a large concentration will undoubtedly affect the crystallization process. We decided to check the influence of hydrogen content on LISPC.

▪ First results related to possible influence of hydrogen on the LISPC process were obtained during experiments on fast LISPC installation (see part AP 3 (a)). Namely, detailed observations of surfaces of the samples after crystallization with light fluxes close and above the optimal values revealed existence of areas with sufficiently different optical contrast, i.e. brighter and darker locations (see Fig. 10 (b)). Raman spectra detected from the locations with different contrast showed the Si-nc peaks with nearly same amplitude and FWHM, but with different spectral positions (Fig. 10 (a)). Namely, the peak maximum detected from the bright location "A" in Fig. 10 (b) was positioned at 0.85 cm^{-1} larger wavenumber than that from darker location "B". This difference in spectral positions suggests that the

tensile stress in the location "A" was less by ~ 420 MPa than that in "B". Additional investigations will be necessary to determine the proper reason for the differences. At the first glance the effect seems to be related to detachment of the MQW film from the substrate. Possible reason for the detachment could be related to intensive hydrogen outgassing of the material during fast LISPC process. During crystallization, hydrogen escapes from the Si film and may even cause bowing of the film surface at the substrate/film interface.

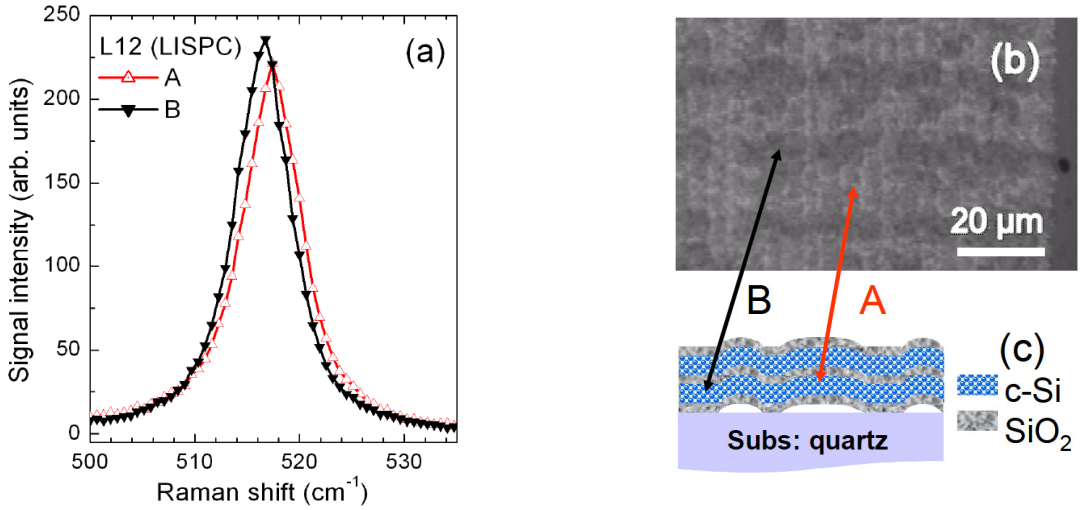


Fig.10. *Raman peaks of Si-nc (a) detected from L12 (MQW: 12 × (Si 5nm+SiO_2 3 nm) crystallized sample in locations A and B shown in the microscopic image of the sample surface in (b). Proposed model (not to the size) of the MQW structure with two Si/SiO_2 periods (for simplicity) explaining origin of difference in the stress values is presented in (c).*

▪ In our joint investigation with SINOVA project partners from Interdisziplinäres Zentrum für Materialwissenschaften (Martin-Luther-Universität Halle-Wittenberg), based on the analyses of the RAMAN and HRTEM results from the same light-crystallized samples, it was suggested that hydrogen atoms during fast effusion through the lattice may cause softening of the Si bonds in a-Si and facilitate LISPC process.

▪ To check the importance of presence of hydrogen atoms in the samples for LISPC we compared crystallization results for as-deposited MQW sample and that subjected to extended (24 hour) annealing in nitrogen at 450ºC. The extended annealing is known to cause full outgassing of hydrogen from the thin MQW film. The Raman spectra of the as-deposited and annealed samples did not differ, however measured absorbance at 532 nm wavelength in the annealed sample was ~1.37 times stronger. The light-induced crystallization experiments showed that the efficiency of LISPC estimated from eq. (1) for the as-deposited sample was ~1.4 times larger in comparison to the annealed sample. These results support the supposition that hydrogen atoms dissolved in the Si layers facilitate the LISPC process.

▪ ***Summarizing,*** hydrogen atoms dissolved in MQW film during the film deposition process strongly affect LISPC process. Namely, the efficiency of LISPC decreases with decrease of hydrogen content and the residual compressive stress decreases. Hydrogen atoms are also considered as possible reason for softening of Si lattice immediately before LISPC.

The results of this investigation were published or submitted, resp., in the journals:

T. Mchedlidze, T. Arguirov, and M. Kittler, "Fast light-induced solid phase crystallization of nanometer thick silicon layers on quartz", SOLID STATE PHENOMENA Volume 178-179, pp. 110-115 (2011).

M. Schade, T. Mchedlidze, M. Kittler and H. S. Leipner, „Light induced crystallization of an amorphous silicon film embedded between silicone oxide layers", THIN SOLID FILMS, submitted (September 2011).

AP 3.1 (d) Further development and optimization of light-induced crystallization, fundamental aspects: LISPC in SiC/$SiO_{1.2}$ hetero-superlattice on glass.

▪ The investigations were performed in cooperation with our project partners from IEK-5 Photovoltaik, Forschungszentrum Jülich. The Partners were working on the concept of application of SiC/SiOx (X<2) hetero-superlattice (HSL) for third generation photovoltaic cells. The concept is based on formation of Si-nc quantum dots in the SiC/SiOx multilayer structure and application of this structure as an absorber in future solar cells. The traditional approach for the formation of Si-nc quantum dots is based on the annealing of HSL consisting from nm thick SiC and SiOx layers at 1050ºC for 1h. We tried to apply light-induced crystallization for formation of Si-nc dots.

▪ The HSL sample contained 20 pairs of 2 nm thick SiC and 5 nm $SiO_{1.2}$ layers (HSL: 20 × (2 nm SiC + 5 nm SiO_2)) deposited on fused silica substrate using PECVD. Pristine location of the sample showed Raman spectra characteristic for unsaturated silicon oxide, with broad band heaving maximum at a spectral position of ~465 cm^{-1}. Increase in the power of the Raman probing beam caused appearance of the Si-nc peak in the spectra. These observations showed that LIC was possible for the HSL structure and further experiments were performed using installation for fast LISPC (see part AP 3 (a)).

▪ Locations with bright and dark image were observed on the sample surface after light treatment. The spectra for these locations differed, namely strong Si-nc peak at ~ 520 cm^{-1} was observed for bright locations, while much weaker peak from supposedly large Si crystallites, with sizes >20 nm, were observed from dark locations. The spectra for the bright locations also contained a couple of

broad peaks at ~1340 and ~1600 cm^{-1}. The last two peaks were identified to originate from so-called "glassy carbon", a phase of amorphous SiC (see e.g. [Y. Inoue, et al., Sol. St. Commun. 48, 1071 (1983)]).

▪ Change in P_{LAS} caused two effects. First, the spectra for the bright locations responded to the increase in P_{LAS} similarly to the response of a-Si layers in Si/SiO_2 MQW, i.e. there was found optimal power for maximal Si-nc signal intensity. Second, the fraction of dark locations gradually increased with P_{LAS} until filling the treated area almost entirely. For estimating the fraction of Si-nc material the intensity of the Si-nc signal registered from the bright locations were multiplied by the fraction of the bright "material". The results suggest that the optimal conditions for the formation of Si-nc correspond to ~0.5 MW/cm^2 flux of light.

▪ Formation of the crystalline SiC was not detected even for the highest used P_{LAS}. Moreover, the signal from glassy carbon seemed to correlate with Si-nc signal in intensity in the most cases. From the shape of the a-SiC peaks and based on the publications (see e.g. [Y. Inoue, et al., Sol. St. Commun. 48, 1071 (1983)]) it was possible to estimate temperature value for formation of Si-nc as 800 - 1000ºC. The dark locations seem to present SiO_2 volumes, maybe containing also high concentration of carbon. Large Si clusters in these volumes were formed by the phase separation mechanism.

▪ ***Summarizing,*** experiments with light-induced crystallization of $SiC/SiO_{1.2}$ HSL on glass showed promising results for formation of Si nanodots in the material. The process of crystallization strongly depends on P_{LAS} and may be optimized for necessary volume fraction, size and distribution of Si nanodots.

AP 3 (a) Development of technique and investigation of conditions for practical application of light-induced crystallization: construction of an installation with advanced LISPC capabilities.

Previous progress in verifying and investigation of LISPC process was achieved applying the setup of Raman instrument for the crystallization. The advantage of such a combination was a possibility of almost real-time observation of the crystallization process applying capabilities of the Raman method. On the other hand the diameter of the light spot in the Raman installation was ~1 μm that prevented possibility for crystallization of large areas, applicable for the electrical measurements. Moreover, due to very short optical focal distance of the installation (<1 mm) and due to vibrations during scan of the sample, substantial variations of the light power density were unavoidable. This caused significant variations in the crystallization quality.

The parameters of the installation applicable for relatively large area LISPC could be summarized as follows:

- Light spot diameter: 5-15μm.
- P_{LAS} up to 2 W.
- Optical focal distance >10 mm
- Scanning speed: 0.1 – 0.3 mm/sec.

For the basis of the installation we used Cascade Prober (model "Summit 12000B-S") which allows precise positioning and scanning. We used frequency doubled Nd:YVO_4 laser producing cw radiation at 532 nm as a light source. Maximal available P_{LAS} was 2.4 W. Optical system was assembled from the separate parts and allowed focusing of the light beam to a spot with diameter 5-40 μm at optical focal distance of 8-15 mm. The process can be controlled by video camera in real time. Control of sample movement and laser parameters were performed from PC. In Fig. 11 the image of the installation with explanations for the parts is presented. For controlling static temperature of the sample and ambient during the crystallization Oxford cryostat can be mounted under the focusing system (see Fig. 11 (b) 5).

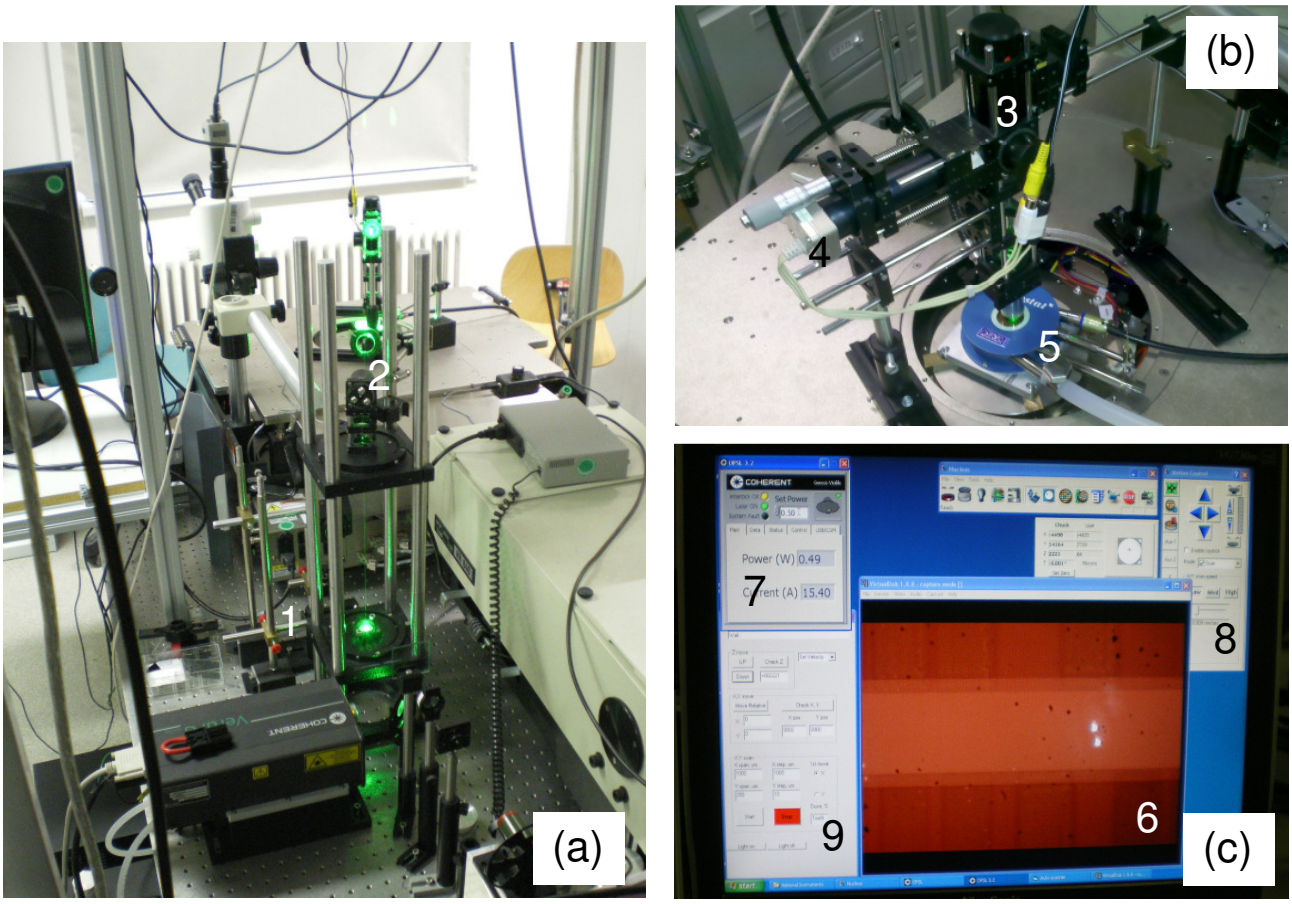


Fig.11. *New installation for LISPC, rear (a) and front (b) views and process control and monitoring screen (c). 1-Laser; 2 - beam guiding system; 3 – focussing and monitoring system; 4 – video*

camera; 5 –cryostat; 6 – image of the sample; 7 – window for control of laser parameters; 8 – Control of prober parameters; 9 – window for control of scanning parameters.

The experiments using the new installation show very promising results. Applying the installation it was possible to crystallize stripes with area up to several mm^2 of the samples in reasonable time. The crystallized stripes show homogeneous image. The Raman spectrum from the crystallized location showed peak of crystalline Si with $F_{CR} \approx 100\%$ for optimal conditions of LISPC. The achieved rate for the LISPC process is 5×10^{-3} mm^2/min. For comparison, in the previous setup the LISPC rate was $< 1\times10^{-7}$ mm^2/min.

▪ ***Summarizing,*** the prototype of the installation for fast LISPC process was constructed. The achieved parameters of the installation allowed homogeneous crystallization of the MQW samples and thin Si films. The LISPC process can be monitored and controlled applying the constructed installation and software.

The results of this investigation were published in the journal:

T. Mchedlidze, T. Arguirov, and M. Kittler, "Fast light-induced solid phase crystallization of nanometer thick silicon layers on quartz", SOLID STATE PHENOMENA Volume 178-179, pp. 110-115 (2011).

AP 3 (b) Development of technique and investigation of conditions for practical application of light-induced crystallization: influence of ambient, gas pressure and temperature on LISPC of Si/SiO_2 MQW on glass.

▪ An ambient and pressure could supposedly influence LISPC process in several ways. First, oxygen atoms in ambient can influence the oxidation of Si material of MQW at high temperatures. Gas pressure or liquid ambient may influence the heat exchange during the crystallization process. Starting temperature determines the value of light flux, which will be necessary for LISPC, thus affecting the efficiency of the process.

▪ It was technically difficult to try experimentally all possible variations. For these series of experiments the sample MQW: 6×(10nm Si+3nm SiO_2) was placed inside Oxford cryostat (see Fig. 11 (b)). It was possible to increase temperature of the sample to 400 K. It was also possible to pump the cryostat to 0.2 mbar pressure and to fill the cryostat with nitrogen at atmospheric pressure instead of air.

▪ To investigate the influence of oxygen on the outcome of the LISPC process, the MQW film on crystalline quartz was treated in air ambient and in nitrogen at normal pressure. The experiments gave insignificant difference. Namely, for optimal LISPC conditions efficiency evaluated by eq. (1) of the process conducted in nitrogen was 1.05 times higher and the residual compressive stress was less in this case by ~ 300 MPa. Therefore we can conclude that oxygen from the ambient at normal pressure participates in the oxidation processes inside the film, however this effect is not decisive at optimal LISPC conditions.

▪ Influence of heat exchange during LISPC was checked by placing the MQW film in water ambient during the crystallization process. The experiments showed worsening of the outcome. Namely, P_{LAS} necessary for the optimal LISPC increased ~2.3 times, thus lowering the efficiency. The experiment was burdened by massive outgassing from the MQW film during crystallization process.

▪ The LISPC experiments conducted in vacuum (at 0.2 mbar) did not show much difference in efficiency of LISPC, suggesting that in the case of gaseous ambient the main heat transfer proceeds through the substrate. However, at $P_{LAS}>P_{OPT}$ the surface of the samples occasionally looked damaged, i.e. small craters with diameter < 0.5 μm appeared on the film surface. We suppose that appearance of the craters may be related to the intensive outgassing during the crystallization.

▪ For estimation of an influence of starting temperature on the LISPC process we can use eq. (2) and assume that the final temperature should be the same (~1550 K) for the optimal LISPC process. To obtain the same final temperature, optimal laser power should be varied, i.e. should decrease with the increase of the staring temperature. As an example, from eq. (2), the ratio $P_{OPT}(300\ K)/P_{OPT}(400\ K)$ should be 1.08 in the assumption of the same final temperature. According to eq. (2), the efficiency also should increase with increase in the starting temperature. Present installation allowed us to rise the starting temperature to 125ºC. The obtained ratio of efficiencies $\eta(125ºC)/\eta(25ºC)$ was ~1.16 in good correspondence with the expected value.

▪ ***Summarizing,*** the experiments with ambient and temperature variations showed broad possibilities to control LISPC process and to further optimize the conditions for crystallization of MQW samples and thin Si films.

GENERAL SUMMARY

➢ Nanometer thick Si films were characterized by Raman spectroscopy and scanning probe microscopy methods. The results were compared to high-resolution transmission microscopy results. All methods showed very close characteristics for the structure of the material.

- The process of light-induced solid phase crystallization of nanometer-thin Si films was investigated and a model of the process was proposed. The model well describes dependence of the process on illumination wavelength and power, on thermal properties of substrate, on starting temperature and other parameters.
- The prototype of the installation for fast LISPC process was constructed. The achieved parameters of the installation allowed homogeneous crystallization of the MQW samples and thin Si films for the areas up to several mm^2.

Berichtsblatt

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3a. Titel des Berichtes
Schlussbericht zum BMBF-Verbundprojekt: **„Siliziumbasierte nanostrukturierte Dünnschichtmaterialien als innovative funktionale Elemente für hocheffiziente Solarzellen der nächsten Generation (SINOVA)“**
Teilvorhaben: **„Lichtinduzierte Kristallisation und Charakterisierung von Si-Nanostrukturen“**

3b. Titel der Veröffentlichung (eines Teils der Ergebnisse des Teilprojektes)
„Light induced solid-phase crystallization of Si nanolayers in Si/SiO_2 multiple quantum wells”
Journal of Applied Physics 107, 124302 (2010)

4a. Autoren des Berichtes **Mchedlidze, Teimuraz; Kittler, Martin** 4b. Autoren der Veröffentlichung **Mchedlidze, Teimuraz; Arguirov, Tzanimir; Kouteva-Arguirova, Simona; Kittler, Martin**	5. Abschlussdatum des Vorhabens **Februar 2012** 6. Veröffentlichungsdatum* **16. Juni 2010** (online) 7. Form der Publikation* **Artikel in Fachzeitschrift**
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16. Zusätzliche Angaben
Einschließlich der oben angegebenen Arbeit in J. Appl. Phys. 107, 124302 (2010) wurden aus dem Teilvorhaben heraus 5 Arbeiten publiziert; eine weitere befindet sich im Begutachtungsprozess.

17. Vorgelegt bei (Titel, Ort, Datum), eines Teils der Ergebnisse des Teilprojektes
10^{th} International Workshop BIAMS 2010, Halle, Juli 2010

18. Kurzfassung
Das Teilvorhaben „Lichtinduzierte Kristallisation und Charakterisierung von Si-Nanostrukturen“ war Bestandteil des Verbundprojektes SINOVA. Si-Schichten in multiplen Quantumwells mit Schichtdicken von einigen Nanometern wurden mit Ramanspektroskopie, Methoden der Scanning Probe Spectroscopy und anderen Verfahren untersucht. Die dabei gewonnenen Ergebnisse wurden mit Untersuchungen verglichen, die von Verbundpartnern mit Hochauflösungs- und analytischer Elektronenmikroskopie vorgenommen wurden. Die benutzten Methoden lieferten (weitgehend) übereinstimmende Aussagen. Der Prozess der lichtinduzierten Kristallisation an Si-Schichten in multiplen Quantumwells mit Schichtdicken von einigen Nanometern wurde detailliert untersucht. Es wurde ein Modell vorgeschlagen, das die Abhängigkeit von der Wellenlänge und Intensität des verwendeten Lichtes, von den thermischen Eigenschaften des benutzten Substratmaterials, von der Starttemperatur und von weiteren Parametern beschreibt. Ein Laboraufbau für die lichtinduzierte Kristallisation wurde realisiert. Damit war es möglich, eine homogene Kristallisation der Si-Schichten in multiplen Quantumwells für Flächen von einigen mm^2 vorzunehmen.

19. Schlagwörter **crystalline Si MQW, thin Si films on quartz, fast solid-phase crystallization by light, crystalline fraction, Raman spectroscopy, scanning probe microscopy, modeling**

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„Light induced solid-phase crystallization of Si nanolayers in Si/SiO_2 multiple quantum wells" Journal of Applied Physics 107, 124302 (2010)

4a. authors of final report **Mchedlidze, Teimuraz; Kittler, Martin** 4b. authors of publication **Mchedlidze, Teimuraz; Arguirov, Tzanimir; Kouteva-Arguirova, Simona; Kittler, Martin**	5. end of project **February 2012** 6. publication date* **16. June 2010** (online) 7. form of publication **journal paper**
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16. supplementary notes

Including the above paper in J. Appl. Phys. 107, 124302 (2010) five papers have been published, reporting results of the sub-project. Moreover, another paper is under revision.

17. presented at (title, place, date), of a part of results of the sub-project

10th International Workshop BIAMS 2010, Halle (Germany), July 2010

18. abstract

The sub-project „Lichtinduzierte Kristallisation und Charakterisierung von Si-Nanostrukturen" was part of the SINOVA project, dealing with novel elements for high-efficient solar cells of next generation. Nanometer thick Si films in multiple quantum wells (MQW) were characterized by Raman spectroscopy and scanning probe microscopy methods. The results were compared to high-resolution and analytical transmission electron microscopy results. All methods showed very close characteristics for the structure of the material. The process of light-induced solid phase crystallization of nanometer-thin Si films was investigated and a model of the process was proposed. The model well describes dependence of the process on illumination wavelength and power, on thermal properties of substrate, on starting temperature and other parameters. The prototype of the installation for fast light-induced crystallization process was constructed. The achieved parameters of the installation allowed homogeneous crystallization of the MQW samples and thin Si films for the areas up to several mm^2.

19. keywords **crystalline Si MQW, thin Si films on quartz, fast solid-phase crystallization by light, crystalline fraction, Raman spectroscopy, scanning probe microscopy, modeling**

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