Aberration-corrected transmission electron microscopy analyses of GaAs/Si interfaces in wafer-bonded multi-junction solar cells

Dietrich Häussler a, Lothar Houben b, Stephanie Essig c, Mert Kurttepeli a, Frank Dimroth c, Rafal E. Dunin-Borkowski b, Wolfgang Jäger a,*

a Institute for Materials Science, Christian-Albrechts-University Kiel, Kaiserstraße 2, 24143 Kiel, Germany
b Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Research Centre Juelich GmbH, 52425 Juelich, Germany
c Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstraße 2, 79110 Freiburg, Germany

Available online 20 July 2013

Keywords:
Multi-junction solar cell
Wafer bonding
Interfaces
Aberration corrected STEM/EELS

1. Introduction

Multi-junction solar cells are of particular interest since efficiencies well above 40% have been obtained for concentrator solar cells which are based on III-V compound semiconductors on Ge substrates [1,2]. The conversion efficiency of solar cells is considered to be decisive for reducing the electricity generation costs by photovoltaics [3]. For silicon as the most widely used semiconductor, considerations of lattice mismatch and differences of lattice constants, thus avoiding defect formation in the active parts of the solar cells is of particular importance since efficiencies well above 40% have been obtained for concentrator solar cells which are based on III-V compound semiconductors. In this methodologically oriented investigation, we explore the potential of combining aberration-corrected high-angle annular dark-field STEM imaging (HAADF-STEM) with spectroscopic techniques, such as EELS and energy-dispersive X-ray spectroscopy (EDXS), and with high-resolution transmission electron microscopy (HR-TEM), in order to analyze the effects of fast atom beam (FAB) and ion beam bombardment (IB) treatment on the structure and composition of bonding interfaces of wafer-bonded solar cells on Si substrates. Investigations using STEM/EELS are able to measure quantitatively and with high precision the width and the fluctuations in element distributions within amorphous interface layers of nanometer extensions, including those of light elements. Such measurements allow the control of the activation treatments and thus support assessing electrical conductivity phenomena connected with impurity and dopant distributions near interfaces for optimized performance of the solar cells.

© 2013 Elsevier B.V. All rights reserved.

Aberration-corrected scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) investigations have been applied to investigate the structure and composition fluctuations near interfaces in wafer-bonded multi-junction solar cells. Multi-junction solar cells are of particular interest since efficiencies well above 40% have been obtained for concentrator solar cells which are based on III-V compound semiconductors. In this methodologically oriented investigation, we explore the potential of combining aberration-corrected high-angle annular dark-field STEM imaging (HAADF-STEM) with spectroscopic techniques, such as EELS and energy-dispersive X-ray spectroscopy (EDXS), and with high-resolution transmission electron microscopy (HR-TEM), in order to analyze the effects of fast atom beam (FAB) and ion beam bombardment (IB) treatment on the structure and composition of bonding interfaces of wafer-bonded solar cells on Si substrates. Investigations using STEM/EELS are able to measure quantitatively and with high precision the width and the fluctuations in element distributions within amorphous interface layers of nanometer extensions, including those of light elements. Such measurements allow the control of the activation treatments and thus support assessing electrical conductivity phenomena connected with impurity and dopant distributions near interfaces for optimized performance of the solar cells.

1. Introduction

Multi-junction solar cells are of particular interest since efficiencies well above 40% have been obtained for concentrator solar cells which are based on III-V compound semiconductors on Ge substrates [1,2]. The conversion efficiency of solar cells is considered to be decisive for reducing the electricity generation costs by photovoltaics [3]. For silicon as the most widely used semiconductor, efficiencies up to 43.5% are only achieved with multi-junction devices made of III-V compound semiconductors [2]. Significantly higher efficiencies up to 43.5% are only achieved with multi-junction devices made of III-V compound semiconductors [2]. State-of-the-art multi-junction solar cells are made of lattice-matched GaInP/GaInAs/Ge and reach solar electric conversion efficiencies up to 41.6% [4]. These solar cells are widely used in space and in terrestrial concentrator systems. Multi-junction solar cells based on crystalline silicon and III-V semiconductors show improved conversion efficiency as compared to single-junction Si cells since the visible wavelength range of the solar spectrum is converted more efficiently by adding additional p-n junctions. Such approaches can reduce the cost of the solar cell device and achieve even higher theoretical efficiencies than the conventional lattice-matched triple-junction solar cell on germanium [5]. The composition of the ternary compounds can be chosen to obtain the desired electronic band gap. The interfaces between the different layers play an important role since they determine the quality of the series connection of the different cells.

Successful concepts for multi-junction cells are monolithic systems which are grown on a Ge or a Si substrate wafer. The heteroepitaxial growth on these substrate materials can be accomplished by (nearly) lattice-matched and by metamorphic growth concepts. High quality and low defect density can be achieved in the heteroepitaxy of III-V compounds on Ge and on Si by applying buffer concepts which aim at accommodating differences of lattice constants, thus avoiding defect formation in active regions of the solar cells. Successful examples are adding appropriate fractions of alloying elements, such as In [6], or introducing nitride layers into the layer stack to hinder dislocations from threading into the active parts of the solar cells [7]. Excellent efficiencies have been obtained by Fraunhofer ISE (Germany) with a Ga0.35In0.65P/Ga0.83In0.17As/Ge metamorphic solar cell which yields...
an efficiency of 41.1% \cite{8,9}. Similar concepts of heteroepitaxial growth of GaInP/GaAs on Si substrates lead to a conversion efficiency of 16.4% (one sun spectrum AM1.5g) \cite{10}.

The difficulty in the fabrication of GaInP/GaAs/Si multi-junction solar cells arises from the different lattice constants and thermal expansion coefficients of GaAs and silicon \cite{11}. Direct growth of the GaInP/GaAs cells on silicon by MOVPE at temperatures from 550 °C to 700 °C can lead to dislocations, antiphase domains \cite{12} or even cracks \cite{13} formed during the cooling phase of the fabrication. Such defects can act as recombination centers in a solar cell, reducing its efficiency.

Another concept for overcoming the constraints of lattice mismatch in the heteroepitaxy for solar cells is the concept of wafer bonding \cite{14}. Fabrication by room-temperature surface-activated wafer bonding can overcome the problems outlined above, resulting in solar cells for which the formation of lattice-mismatch induced defects in the active solar cell layers is substantially reduced or completely avoided. The upper GaInP/GaAs dual-junction solar cells are grown lattice-matched on GaAs substrates before they are transferred and bonded to the silicon bottom cell. This fabrication process enabled a GaInP/GaAs/Si multi-junction solar cell efficiency of 23.6% \cite{5}.

High-resolution methods of transmission electron microscopy (TEM) offer tools for defect and interface studies that are capable of providing routinely quantitative structural information on the atomic scale \cite{15}. The successful introduction of aberration-corrected electron lenses in TEM instruments \cite{16,17} that initiated a new generation of aberration-corrected instruments has lead to completely novel possibilities for ex-situ and in-situ TEM experiments for materials research and for life science. Beneficial is not only the largely improved resolution but also the possibilities for quantitative measurements at high precision. The huge progress that these instruments provide for the application of various methods of TEM to current problems of condensed matter physics and materials research is described in various reviews \cite{18–23}. Aberration-corrected scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) investigations are particularly well suited for measuring compositional changes, electronic structure and bonding of interfaces \cite{18,22}. The attainable resolution using aberration-corrected optics is on the atomic scale, limited only by the probe propagation in the sample and the scattering cross-section of the inelastic scattering event. The rapid progress in the field is documented in compelling examples of atomic scale chemical mapping predominantly on perovskite structures, e.g. in \cite{24–27} and of single atom spectroscopy \cite{28,29}.

In our investigations we use aberration-corrected STEM and EELS to examine the structure and element distribution near interfaces of wafer-bonded crystalline GaInP/GaAs/Si multi-junction solar cells. The measurements are compared with cross-section high-resolution TEM (HR-TEM) and energy-dispersive X-ray spectroscopy (EDXS) line profile analyses of the wafer-bonded interface. For the wafer-bonded cells, the morphology, structure and element distribution around the interface between GaAs and Si is decisive for the control of the electrical properties and thus the performance of the multi-junction cells. Specifically, the effect of activation treatments prior to the wafer-bonding has been examined.

2. Experimental procedures

2.1. Fabrication of solar cells

A 10 μm thin GaInP/GaAs dual junction solar cell structure was grown lattice-matched on a GaAs substrate by metal organic vapor phase epitaxy (MOVPE, \cite{30}) at Fraunhofer ISE. The solar cells were transferred to Si by surface activated direct wafer bonding (schematic, Fig. 1). Bonding was performed in a SAB-100 vacuum chamber from Ayumi. A typical layer sequence for a GaInP/GaAs/Si solar cell is given in \cite{5}.

An essential stage of the bonding process represents the “activation” of the surfaces by particle bombardment (schematic, Fig. 1). This processing step aims at cleaning and surface de-oxidation before bonding under high vacuum conditions. We have investigated two alternative activation concepts, ion beam bombardment (IB) treatment and fast atom beam (FAB) treatment. The FAB activation uses argon atoms which, sequentially, were first ionized, then accelerated by a voltage of 1000 V, and finally neutralized. The atom beam sources apply graphite aperture plates which serve for shaping the Ar beam. The FAB method has been successfully used also for the bonding of other semiconductor systems \cite{31,32}.

The Ar ions used for the IB activation were accelerated with a voltage of only 100 V. The argon atoms and ions, respectively, reach the surfaces under an angle of approximately 45°.

2.2. Characterization

The bonding interface between the GaAs middle-cell and the Si bottom-cell and the regions in the vicinity of the interfaces have been characterized by STEM imaging and elemental mappings in STEM-EELS and compared with high-resolution TEM (HRTEM) and with energy-dispersive X-ray spectroscopy (EDXS) line scan analyses. The experiments were conducted on cross-section specimens prepared by standard ion milling and subsequent cleaning procedures.

The STEM-EELS investigations have been largely carried out using a probe corrected FEI Titan 80-300 FEG TEM (Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons Juelich) equipped with a CEOS double hexapole corrector at an acceleration voltage of 300 kV. The aberrations up to third order were corrected to small values, eliminating resolution limiting aberration effects within the illumination aperture of 25 mrad radius, resulting in a probe diameter better than one-tenth of a nanometer. The probe current for the STEM–EELS experiments was varied between 60 pA for low energy loss

---

![Image](image-url)
recordings and 250 pA for core-loss recordings. EELS spectra were acquired with a collection angle of 34 mrad. For both the FAB and the IB treatments, the elements In, P and Ar (if present) are not detected at the interfaces due to detection sensitivity limits (Fig. 6). Similarly, the elements Fe, Cr, Ni, Mn, and Co which are detected at the interface for the IB treatments are all below the detection sensitivity for the FAB-treated bond interfaces (Fig. 6). The presence or absence of these elements is discussed in Ch. 4.2 and related to the bond surface activation treatment.

The element profiles are obtained from characteristic core loss signals after background subtraction and subsequent normalization to an appropriate double differential scattering cross-section obtained from a Hartree–Slater calculation. The EELS signals reflect the areal number density of atoms in the sample volume probed by the STEM beam, assuming that the sample thickness near the interface is constant. The effective area for this normalization depends on the composition via the beam broadening (or the interaction volume). Furthermore, the angular scattering distributions for different elemental compositions will be different. These phenomena aggravate a normalization which would be desirable for obtaining a total concentration. Therefore the data are related to an areal density. The error bars given in the Fig. 6 indicate the 68% signal uncertainty due to detection noise, signal noise and background extrapolation error.

The HRTEM studies and the EDXS line profiling in STEM mode have been performed using a TECNAI F30 G2 at 300 kV equipped with an EDAX system (CAU Kiel). The EDXS profiles across the GaAs–Si bonding interfaces were obtained with a beam diameter of about 1 nm. The corresponding profiles (Figs. 2b, 3b) are not deconvoluted with respect to the expected excitation volumes. There are slight differences between these line scan profiles due to differences in the step widths and the ranges chosen during the experimental acquisition.

3. Experimental results

3.1. HRTEM and EDXS line scan analyses

The HRTEM imaging of the cross-section samples reveal that the two different activation treatments lead to similar structures of the bonding interfaces. For both treatments amorphous interlayers with a thickness of a few nanometers are formed at the bond interfaces. The amorphous interlayers are rather uniform in thickness (Figs. 2a, 3a). The interfaces between the amorphous interlayers and the crystalline Si regions and crystalline GaAs regions are largely flat over larger distances and are, on a local scale, atomically sharp (Figs. 2a, 3a). The adjacent Si substrate and GaAs layer regions appear to be locally strained but largely free of extended defects. In the projections depicted by Figs. 2 and 3, the lattice images reveal nearly epitaxial orientation relationships between the lattices of Si and GaAs.

Figs. 2b and 3b depict the elemental composition profiles across the bonding interfaces as revealed by the EDXS line scan analyses. The comparison shows qualitatively similar concentration distributions for Ga, As, and Si across these interfaces. Fig. 2b shows a small increase of the O–K signal near the amorphous layer. This increase has been measured reproducibly several times.

3.2. Aberration-corrected STEM investigations

As an overview, Fig. 4 shows the STEM HAADF images of the solar cell cross-sections, the bonded GaAs–Si interface, and the crystalline lattice of the Si solar cell next to the interface in a <110> lattice projection. For both the FAB and the IB case, there exists an interface layer whose extension is of the order of few nanometers. The dimensions of these layers are comparable with the dimensions of amorphous interface layers at bonding interfaces reported earlier [33]. By comparing the average HAADF contrast of these interface layers with each other (Figs. 4, 5) it becomes obvious that the contrast is brighter for the interface layer resulting from IB treatment (Figs. 4b, 5b). The contrast modulation within the GaAs region is related to the typical layer sequence chosen for the GaInP/GaAs/Si solar cell, including a layer system that is used as tunnel diode for the series connection of the adjacent subcells (see [5] for details).

For the FAB and the IB case, Fig. 5 shows enlarged views of the bond interface regions between the GaAs middle-cell and the Si bottom-cell. The cross-section image is taken in a lattice orientation near a Si <110> zone axis and indicates the projected positions of the individual atom columns of the Si lattice. It becomes evident that the local layer widths and the layer morphologies can be determined with precisions on the atomic scale from such cross-section HAADF–STEM images.

3.3. Aberration-corrected EELS analyses

Fig. 6 shows the STEM–EELS profiles of the identical TEM cross-section samples. The EELS profiles for III–V multi-junction solar

![Fig. 2.](image-url) (a) HR-TEM image of the interface wafer-bonded following FAB treatment, showing an amorphous layer and the adjacent crystalline layers. Cross-section imaged near a $<110>$ Si zone axis orientation. (b) EDXS line scans measured across the interface in this region, depicting the Ga–L, As–L, Si–K, and O–K intensities (not quantitative composition values). The black vertical line denotes the averaged center position of the amorphous layer. Relative measurements.
cells wafer-bonded on Si after fast atom bombardment treatment and after IB treatment are taken across the bonding interface. The EELS profiles exhibit signal intensities after background subtraction and normalization to the inelastic scattering cross-section. Error bars reflect the 68% confidence interval for the signal calculated as the combined effect of signal noise, background extrapolation error and detection noise. The analyses of the element distributions clearly benefit from the reduced probe size and the unmatched beam current density of an aberration-corrected optical set-up in STEM. The high spatial resolution on the sub-nanometer scale allows us to determine the composition fluctuations within the amorphous interface layers that are present in the wafer-bonded GaAs–Si junctions.

Fig. 6(a) and (b) shows the elemental profiles of Ga, As and Si for FAB and IB activation treatment. The distributions of several elements, including O, C, In, P, Ar, Fe, Cr, Co, Mn, and Ni, were evaluated for both cases. Fig. 6(c) and (d) shows the presence of those elements that could be detected with significance. The detection limit for the spatially resolved measurement of minor concentrations of elements depends in general on the differential scattering cross-section for the characteristic energy loss and the combined uncertainty due to signal and detection...
noise. A coarse estimate of the detection limit is in the range of a few atom percent for the present measurements. The comparison shows that the interface sharpness of the concentration profiles for Ga, As, and Si are different for the two cases, with a smoother transition for the FAB treatment (Fig. 6a, b).

The FAB-activated wafer-bonding resulted in an oxygen-rich interface (Fig. 6(c)). The true sub-nanometer resolution obtained by the analysis with an aberration-corrected probe allows identifying an oxygen-rich double layer that is manifested by the two maxima in the O profile with a width of roughly 1.0 nm in Fig. 6 (c) and can be related to residuals of native oxide surface layers (see discussion in Ch. 4.2). Accordingly, the Ga profile in Fig. 6(a) is slightly shifted with respect to the As profile, by 1.2 nm. The obvious dip in the oxygen profile is connected with a smooth reduction in the HAADF signal (not shown here). We conclude that the dip is indicative of the less dense material at the true interface where the wafers are bonded. At this position a small peak of carbon residues is present.

Metallic elements, such as Fe, Cr, Co, Ni, and Mn, are detected at the interface of the IB activated sample. The cumulative number density of atoms of these elements reaches that of the GaAs bulk-like material nearby. The metal containing interface layer between the GaAs and Si is probably metallic since only a minor concentration of O is present as indicated by the weak signal intensity just above detection noise. Unlike the FAB sample the profiles across the interface do not show a pronounced concentration modulation, i.e., the metal composition is rather homogeneous over the width of the interface layer of approximately 2 nm.

Within the measurement precision of a few atomic percent, the elements In, P and Ar were not detectable at the GaAs–Si bond interface, neither for the FAB nor for the IB treatments.

4. Discussion

4.1. Amorphous interlayers at the GaAs–Si bond interface

The amorphous interlayers at the GaAs–Si bond interface are the result of the different activation treatments applied. The amorphous nature of the interface layers is documented convincingly by the contrast behavior observed in the HRTEM images (Figs. 2, 3). The contrast behavior observed by STEM (Fig. 4) is compatible with this conclusion which is indirectly also supported by the results of the spectroscopic EDXS analyses (Figs. 2b, 3b) and EELS analyses (Fig. 6). The HAADF STEM layer contrast reflects via its atom number dependence the spectroscopic results for the elemental composition distributions across the interface (Fig. 5a, b). For the FAB activation the oxygen-rich interface layer depicts low contrast and amorphous appearance whereas for the IB activation the metal containing interface layer shows high contrast. As expected the corresponding HRTEM images show also dark absorption contrast contributions in this case.

4.2. Presence, origin, and role of metals, of oxygen, and of carbon at the interface

Characteristic for the FAB activation treatment is the formation of two ultrathin oxygen-rich layers at the interface which is detected by aberration-corrected STEM–EELS only (Fig. 6c). The STEM–EDXS experiment (Fig. 2b) confirms the presence of O, however, lacks spatial resolution so that the presence of 2 layers cannot be resolved. Before treatment, both the Si and the GaAs wafers had a native surface oxide with a nominal thickness of 1.5–2 nm. The origin of oxygen in the two layers can be attributed to a FAB treatment which, in the case of the chosen sample system, has been applied for an insufficiently long period of time so that not all of the native oxides, such as Ga₂O₃ or As₂O₅, could be removed (compare Fig. 6a with 6c).

In addition, a small amount of C is detected at the interface by STEM–EELS (Fig. 6d) and, EELS only (Fig. 6c). The presence of O, EELS only (Fig. 6c). The presence of O, however, lacks spatial resolution so that the presence of 2 layers cannot be resolved. Before treatment, both the Si and the GaAs wafers had a native surface oxide with a nominal thickness of 1.5–2 nm. The origin of oxygen in the two layers can be attributed to a FAB treatment which, in the case of the chosen sample system, has been applied for an insufficiently long period of time so that not all of the native oxides, such as Ga₂O₃ or As₂O₅, could be removed (compare Fig. 6a with 6c).

In addition, a small amount of C is detected at the interface by STEM–EELS (Fig. 6d). A possible source for C is the use of a graphite aperture characteristic for the IB activation treatment is the presence of considerable amounts of metallic elements at the interface which are detected by aberration-corrected STEM–EELS (Fig. 6d) and, with less spatial resolution, also by STEM–EDXS (Fig. 3b). The metallic contaminants are likely to originate from the ion beam source system used for the bond surface activation by ion beam treatment (and presumably also by the conditions chosen, see Ch. 2.1). The minor concentration of O detected at the interface is likely to originate from residual native surface oxide. The observed contaminants will disturb the current transport across the Si–GaAs interface and thereby influence the performance of the solar cell. Furthermore, metallic impurities diffusing into the Si lattice could lead to reduced cell efficiencies by forming deep electronic donor or acceptor levels which act as traps for charge carriers.
4.3. Comparison of the interface analyses performed by aberration-corrected STEM–EELS and STEM–EDXS

The aberration-corrected STEM–EELS analyses have been successful in detecting phenomena which are not detected by the conventional STEM–EDXS analyses of an instrument whose electron optics is not corrected. Due to the considerably higher spatial resolution and detection sensitivity of an instrument with a corrected electron optics (e.g. cf. Figs. 2, 3 with Fig. 6) detailed and quantitative interface characterizations could be performed that allow correlating the structural and compositional information with the effects of individual steps during the fabrication of wafer-bond interfaces of solar cells. In addition, the STEM–EELS results reflect that the spatial resolution limitations for such interface analyses are solely determined by the electron beam broadening and angular scattering distributions.

The STEM–EDXS analyses (Figs. 2b, 3b) show results that qualitatively are in agreement with the STEM–EELS analyses (Fig. 6) but suffer from a lack of spatial resolution and detection sensitivity. No quantitative conclusion can be drawn with regard to the EDXS detection sensitivity, however, the presence also of light elements at the interface can be detected reproducibly as, for instance, oxygen by the presence of a small X-ray K peak intensity in the spectra. The results for the metallic elements are qualitatively in accordance with the EELS results.

The STEM methods which applied a corrected electron optics have therefore enabled interface analyses that are invaluable for monitoring and control of fabrication processes of solar cells, yielding information that is not accessible by any other analytical technique.

5. Conclusions

Aberration-corrected STEM and EELS investigations, combined with high-resolution TEM, have been applied to investigate the structure and composition of interfaces in wafer-bonded multi-junction solar cells.

The effects of fast atom beam (FAB) and of ion beam (IB) activation treatments on the structure and composition of bonding interfaces of wafer-bonded solar cells on Si substrates can be monitored with high precision and quantitatively in the nanometer-range.

Projected widths of interface layers can be determined on the atomic scale by STEM–HAAADF imaging.

Fluctuations of the element concentrations within amorphous interface layers of nanometer extensions, including light element distributions, are revealed with high precision by EELS measurements. EELS profiles taken across the bonding interface exhibit Si, O, As, and C signal intensities after background subtraction and normalization to the inelastic scattering cross-section.
The FAB-activated wafer-bonding resulted in an oxygen-rich interface layer with minor C contamination. The sub-nanometer resolution obtained by the analysis with an aberration-corrected probe allowed identifying the presence of an oxygen-rich double layer, each of which with a width of roughly 1.0 nm, which is attributed to the chosen condition for bond surface activation treatment.

The IB-activated sample is characterized by a metal containing interface layer between the GaAs and the Si. Substantial amounts of Fe, Cr, Co, Ni, Mn are detected, at a simultaneously minor interface layer between the GaAs and the Si. Substantial amounts of O being just above detection noise. The presence of the metallic contaminants can be attributed to the fabrication conditions chosen for the bond surface activation by ion beam treatment. Such contaminants will disturb the current transport across the Si–GaAs interface, and metallic impurities diffusing into the Si are likely to lead to electrically active impurities reducing the cell efficiency.

In summary, the study confirms that the advanced imaging and spectroscopic methods of aberration-corrected STEM are advantageous for characterizing the morphology, the element distributions, and the structure of layers and interfaces for the monitoring, control, and optimization of different concepts of fabricating high-efficiency solar cells.

Acknowledgments

It is a pleasure to dedicate this paper to our colleagues David J. Smith, W. Owen Saxton, and Dirk van Dyck who shaped with their scientific achievements the understanding of the methods and their impact in material and condensed matter science. One of us (Wolfgang Jäger) would like to thank particularly David Smith for the many stimulating discussions since our first contacts. It is a pleasure to thank the reviewers of the manuscript for their valuable comments.

References