Title: Threading Dislocation Density Characterization in III-V Photovoltaic Materials by Electron Channeling Contrast Imaging

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Abstract: Accurate and rapid threading dislocation density (TDD) characterization of III-V photovoltaic materials using electron channeling contrast imaging (ECCI) is demonstrated. TDDs measured using ECCI showed close agreement with those from electron beam-induced current mapping (EBIC) and defect selective etching (DSE). ECCI is shown to be well-suited for measuring TDD values over a range of $\sim 5 \times 10^6$ to $5 \times 10^8 \text{ cm}^{-2}$. ECCI can distinguish individual dislocations in clusters closer than $0.2 \text{ }\mu\text{m}$, highlighting its excellent spatial resolution compared to DSE and EBIC. Taken together, ECCI is shown to be a versatile and complementary method to rapidly quantify TDD in III-V solar cells.

Keywords: A1. Characterization A1. Defects A3. Molecular beam epitaxy B2. Semiconducting III-V materials B3. Solar cells

1. INTRODUCTION

III-V metamorphic materials are technologically important for solar cells [1-3]. Despite continual improvement in both material quality and device performance, threading dislocations in these materials are unavoidable, and high threading dislocation density (TDD) degrades solar cell efficiency due to non-radiative recombination at dislocations [4, 5]. The ability to accurately quantify TDD is important in achieving lower TDD and higher efficiency in III-V solar cells. Dislocations in III-V metamorphic materials are often inhomogeneously distributed into regions of high TDD (i.e. clusters or pileups) separated by large areas with relatively low TDD [6-9]. This presents challenges for accurate TDD quantification and hinders understanding of the effect of dislocations on device performance.

Plan-view transmission electron microscopy (PVTEM), electron beam-induced current (EBIC), cathodoluminescence (CL), and defect selective etching (DSE) are commonly used to obtain TDD, with well-known advantages and disadvantages (Table 1) [10]. PVTEM has been a commonly used technique due to its ability to clearly distinguish various types of dislocations via two-beam analysis with excellent spatial resolution, while suffering minimally from nanoscale surface roughness [11]. However, PVTEM has difficulty in accurately measuring samples with $TDD \ll 10^7 \text{ cm}^{-2}$ due to the requirement of a large number of images, and, moreover, it is challenging to detect non-uniformly distributed dislocations across length scales (areas) $>100 \text{ }\mu\text{m}$ ($10,000 \text{ }\mu\text{m}^2$) [10]. Additionally, sample preparation for PVTEM is destructive and time consuming. EBIC and CL are scanning electron microscopy (SEM)-based techniques that are accurate over a large range of TDD up to $\sim 5 \times 10^7 \text{ cm}^{-2}$ and capable of sampling solar cell devices nondestructively [10, 12]. However, dark spots for individual dislocations are not easily distinguishable when they occur in clusters or pileups, and samples for EBIC require ohmic electrical contacts. DSE is an economical method able to rapidly analyze areas $>10,000 \text{ }\mu\text{m}^2$. However, errors of 25-50% are possible for samples with $TDD > 10^7 \text{ cm}^{-2}$ due to insufficient resolution, and DSE requires a carefully tested, composition-specific chemical etchant to reliably reveal threads with minimal artifacts [10, 13, 14]. An ideal TDD characterization technique would combine the spatial resolution of PVTEM with the ability to resolve threading dislocations over large areas non-destructively.

Electron channeling contrast imaging (ECCI) is a promising SEM-based technique to measure TDD non-destructively and without sample preparation [15-17]. ECCI uses the changes in back-scattered electron yield at defects close to the surface of a sample ($< 50 \text{ nm}$) to generate contrast [18], and a comparison of ECCI with other techniques is given in Table 1. ECCI does

not require device processing or a specific chemical etchant, unlike EBIC or DSE, respectively, and is effective for indirect-gap materials, unlike CL. ECCI has been used to investigate misfit dislocations in $\text{Si}_{1-x}\text{Ge}_x$, $\text{In}_x\text{Ga}_{1-x}\text{As}$ and GaP/Si [18-21]. Threading dislocations in GaN have been imaged in ECCI and shown to correspond to dislocations seen in CL [15, 22]. However, TDD estimation in III-V solar cells has not been extensively explored using ECCI.

In this work, electron channeling contrast imaging (ECCI) is compared to other TDD characterization techniques in III-V solar cell materials. We demonstrate the flexibility of ECCI by measuring TDD over two orders of magnitude from $\sim 5 \times 10^6$ - $5 \times 10^8 \text{ cm}^{-2}$. Large-area ($\sim 1,000 \text{ } \mu\text{m}^2$) comparisons of TDD values obtained from both EBIC and ECCI in $\text{GaAs}_y\text{P}_{1-y}/\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ solar cells agree to within 15-28%, and small-area, local comparison of individual threads in ECCI with EBIC and DSE showed similar agreement. Finally, ECCI is used to distinguish individual dislocations closer than $0.2 \text{ } \mu\text{m}$, demonstrating the ability to resolve dislocations in clusters and pileups, where local TDD values may exceed 10^9 cm^{-2} .

2. EXPERIMENTAL DETAILS

GaP/Si-based samples were grown in a Veeco Mod GEN-II solid-source molecular beam epitaxy system on GaP/Si (001) templates from NAsP III/V GmbH, as previously reported [23]. $\text{GaAs}_y\text{P}_{1-y}/\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ solar cells were grown by chemical vapor deposition on (001) substrates with 6° offcut towards [110] and fabricated as previously reported [9, 24]. All samples had smooth surfaces with rms roughness $< 10 \text{ nm}$, which is important due to the sensitivity of the ECCI signal to surface roughness; conventional secondary electron SEM images were taken to differentiate the dislocation channeling contrast from surface features [16]. ECCI was performed using a FEI XL 30 SEM operating at an accelerating voltage of 25-30 kV, an approximate beam current of 36.9 nA, and a working distance of 3-6 mm for imaging. The samples were situated

approximately perpendicular to the impinging electron beam, and backscattered electrons were detected by a KE Developments annular, pole-piece mounted backscattered electron (BSE) detector. As described by others [16, 18], the first step in ECCI imaging is to observe the electron channeling pattern that forms due to backscattered electrons diffracting from atomic planes near the surface of the sample, typically under a low magnification $< 10\times$. The sample is subsequently tilted such that a high-symmetry channeling line is at the center of the field of view. In this work, both 400 and 220 conditions yielded strong contrast for threading dislocations [18], which is analogous to the expected contrast from 60° dislocations using similar 2-beam diffraction conditions in PVTEM [11]. Once the electron channeling line is centered, the electron beam is converged to the surface of the sample to image defects at magnifications of 10,000-20,000 $\times$ (individual image areas of 30-150 μm^2). ECCI is very sensitive to the electron channeling conditions [16], and we found very small shifts ($< 0.2^\circ$) from the required channeling condition to minimize or extinguish dislocation contrast due to non-optimized contrast conditions (Fig. 1). While dislocation contrast in PVTEM is also highly sensitive to small deviations from the Bragg condition, the effect is usually to create an unoptimized contrast condition, as opposed to a no-contrast condition [11].

Threading dislocations observed by both DSE and EBIC were locally compared with ECCI. To accomplish this, ECCI imaging was first performed while noting the precise location of the collected images using mechanical scratches as fiduciary markers to allow the exact area to be found in subsequent experiments. For the ECCI-EBIC comparison, EBIC was subsequently performed on the solar cell to correlate the dark spots with the dark-bright spots in ECCI. An indium blob was used for the front contact and silver paste for the back contact of the solar cell. EBIC was performed using a FEI XL 30 SEM operating at an accelerating voltage of 10-15 kV

and an approximate beam current of 2.1-2.5 nA. For the ECCI-DSE comparison, DSE is performed as previously reported [10], and secondary electron SEM images of the etched regions allowed correlation of etch pits with dark-bright spots. For the large-area, statistical comparison of ECCI to EBIC, EBIC maps were collected using an accelerating voltage of 10.5-12.5 kV in the same FEI XL 30 SEM covering at least 1,000 μm^2 areas.

3. EXPERIMENTAL RESULTS AND DISCUSSION

ECCI images for GaP, $\text{GaAs}_y\text{P}_{1-y}$, and GaAs displayed distinct dark-bright spots representing threading dislocations, comparable to previously published ECCI images for other materials [15, 21, 22]. The ability to image dislocations across the whole composition range of $\text{GaAs}_y\text{P}_{1-y}$ is an advantage over DSE, where different compositions of $\text{GaAs}_y\text{P}_{1-y}$ require different etchants with disparate etch rates [10]. Fig. 2 illustrates the versatility of ECCI where samples with TDD varying by over two orders of magnitude are readily imaged. The lines and streaks in Fig. 2 (b) also appear clearly in secondary electron images, and are therefore interpreted as surface artifacts and growth non-homogeneities present on the surface of the sample. As noted above, EBIC and CL cannot be used to measure the high end of TDD (e.g. Fig. 2(d)), since EBIC dark spots have a diameter of ~ 500 nm under typical imaging conditions. In contrast, PVTEM is difficult at the low end of TDD (e.g. Fig. 2(a)) due to the difficulty in preparing and imaging large-area, electron-transparent specimens. However, we have also found that ECCI is difficult for samples with TDD less than those shown in Fig. 2(a), since the dark-bright spots in ECCI become difficult to distinguish from the background at magnifications $< 10,000\times$; for a TDD of $1\times 10^6 \text{ cm}^{-2}$, an ideal field of view would be $> 100 \mu\text{m}^2$ to capture > 1 thread/frame on average, which in turn dictates the use of magnifications $< 10,000\times$. The higher magnification needed in ECCI primarily results from the dark-bright spots having apparent

diameters of ~50-100 nm under typical imaging conditions, ~one fifth of the diameter of dark spots in EBIC.

Conversely, the smaller diameter of spots in ECCI can be advantageous for resolving individual dislocations in clusters or pileup regions, as is common in metamorphic solar cell materials. The two dislocations in Fig. 3 spaced ~0.2 μm apart can be readily resolved by ECCI. This demonstrates the excellent spatial resolution of ECCI, arguably one of its main advantages over other techniques. The resolution of ECCI is suitable for investigating the effect of TDD on solar cell performance in III-V solar cells with non-uniform dislocation pile-ups [6, 25].

We performed additional experiments to check the accuracy of ECCI in TDD quantification over both large areas and in local areas. The statistical comparison of TDD from both EBIC and ECCI in $\text{GaAs}_y\text{P}_{1-y}/\text{Si}_{1-x}\text{Ge}_x$ solar cells showed close agreement with only 15-28% discrepancy over ~1,000 μm^2 (Fig. 4). The TDD obtained from ECCI is consistently higher than EBIC, due to the ability of ECCI to resolve threading dislocations occurring in clusters or pileups, with increasing discrepancy at higher TDD. These results suggest that ECCI is more accurate than other techniques. Local comparison of the same areas in a $\text{GaAs}_y\text{P}_{1-y}/\text{Si}_{1-x}\text{Ge}_x$ solar cell using both ECCI and EBIC showed close agreement with ~15% discrepancy over ~200 μm^2 . Fig. 5 shows a representative comparison of the same ~35 μm^2 area with all 5 spots in ECCI corresponding to dark spots in EBIC. DSE comparison of 500 nm GaP/Si in Fig. 6 further show the accuracy of ECCI in detecting threading dislocations, with only ~17% discrepancy between the 7 spots in ECCI and 6 etch pits. A similar discrepancy between ECCI spots and etch pits was found over ~200 μm^2 (not shown). These results demonstrate that ECCI can be used to measure very similar TDD values to both EBIC and DSE in III-V photovoltaic materials, despite highly different dislocation contrast mechanisms.

4. CONCLUSIONS

ECCI is an accurate technique over a wide range of TDD with the ability to distinguish dislocations in pileups and clusters without any sample preparation. Large-area and local-area comparisons of TDD using EBIC and ECCI in $\text{GaAs}_y\text{P}_{1-y}/\text{Si}_{1-x}\text{Ge}_x$ solar cells showed good agreement, with a consistently higher TDD measured by ECCI due to its ability to resolve dislocations in clusters. Local comparison of TDD using ECCI and DSE further demonstrates the accuracy of ECCI in detecting threading dislocations. ECCI is a complementary method for sampling TDD in III-V photovoltaic materials with clear advantages over other techniques. One challenge of ECCI is the difficulty of measuring TDD values $\leq 1 \times 10^6 \text{ cm}^{-2}$ due to the need for high magnification images (10,000 $\times$) and the small apparent size of dark-bright spots (50-100 nm). A combination of very high resolution imaging with appropriate digital image processing could help to alleviate this challenge.

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Figure captions:

Fig. 1: (a) Threading dislocations observed by ECCI in a GaP/Si sample. (b) Threading dislocation contrast disappears or minimizes due to a 0.2° tilt away from the electron channeling condition in (a). Insets are electron channeling patterns captured at low magnification showing how the samples were oriented for each ECCI image.

Fig. 2: Typical $10,000\times$ ECCI images of (a) $\text{GaAs}_y\text{P}_{1-y}/\text{Si}_{1-x}\text{Ge}_x$ solar cell in region of low local TDD (b) $\text{GaAs}_y\text{P}_{1-y}/\text{Si}_{1-x}\text{Ge}_x$ solar cell in region of high local TDD (c) 500 nm GaP/Si in region of high local TDD, and (d) GaAs directly on GaP with high TDD. ECCI works over a wide range of TDD from $\sim 5\times 10^6$ to $\sim 5\times 10^8 \text{ cm}^{-2}$.

Fig. 3: $50,000\times$ ECCI image of GaAs directly on GaP. ECCI is able to clearly distinguish dislocations $\sim 0.2 \text{ }\mu\text{m}$ apart.

Fig. 4: Large-area comparison of TDD from both EBIC and ECCI in $\text{GaAs}_y\text{P}_{1-y}/\text{Si}_{1-x}\text{Ge}_x$ solar cells showed agreement to within 15-28%, with increasing discrepancy at higher TDD due to better ECCI resolution. Total area surveyed per data point was $\sim 1,000 \text{ }\mu\text{m}^2$.

Fig. 5: Representative local-area comparison from a $\text{GaAs}_y\text{P}_{1-y}/\text{Si}_{1-x}\text{Ge}_x$ solar cell showing (a) $10,000\times$ ECCI image and (b) $10,000\times$ EBIC image.

Fig. 6: Representative local-area comparison from a 500 nm GaP/Si sample showing (a) $10,000\times$ ECCI image and (b) $10,000\times$ defect selective etching (DSE) pit pattern.

	Planar-view transmission electron microscopy (PVTEM)	Electron beam-induced current mapping (EBIC) /Cathodo-luminescence (CL)	Defect selective etching (DSE)	Electron channeling contrast imaging (ECCI)
Area per picture (μm^2)	~10-100	~1,000-10,000	~10,000	~30-150
Destructive?	Yes	No	Yes	No
TDD range (cm^{-2})	$>1 \times 10^6$	$1 \times 10^4 - 1 \times 10^8$	$1 \times 10^4 - 1 \times 10^7$	$5 \times 10^6 - 5 \times 10^8$
Detection of threading dislocations	Direct identification of threading dislocations using strain contrast	Dark spots correspond to strong non-radiative recombination at electrically active dislocations	Selectively higher chemical attack rate at dislocations leads to etch pit formation	Dislocation strain field locally alters electron channeling, leading to dark-bright contrast
Key advantages	Well-established, excellent spatial resolution	Samples large solar cell areas rapidly	Rapid and economical technique	No device processing or material-specific chemicals required
Key limitations	Limited total area	Requires device processing for EBIC, direct-gap for CL	Specific chemical etchant required	Precise tilt conditions required for high resolution images
Equipment required	TEM and sample preparation equipment	Junction with ohmic contacts and scanning electron microscope (SEM) with electrical feedthrough for EBIC. SEM with optical detection system for CL	Hot plate and phase contrast microscope	SEM with backscatter detector

Table 1: Table comparing ECCI to other common characterization techniques.

Figure(s)

(a)

$g=(022)\uparrow$

$\text{TDD}=3\times 10^6\text{ cm}^{-2}$

(b)

$g=(022)\uparrow$

$\text{TDD}=1\times 10^7\text{ cm}^{-2}$

(c)

$g=(022)\uparrow$

$\text{TDD}=3\times 10^7\text{ cm}^{-2}$

2 μm

(d)

$g=(022)\uparrow$

$\text{TDD}=4\times 10^8\text{ cm}^{-2}$

(a)

$g=(022)\uparrow$

(b)

2 μm