# Crystalline and electrical characteristics of $C_{60}$-doped GaAs films

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**Abstract**

$C_{60}$ uniformly doped and δ-doped GaAs layers are grown by migration enhanced epitaxy method. Crystalline and electrical characteristics of the layers are investigated by reflection high energy electron diffraction, X-ray diffraction and capacitance-voltage measurements. $C_{60}$ high-concentration doping is found to introduce 2D defects, and X-ray diffraction pole-figure measurements show that the rotational domains appear predominantly on {111}A plane. This indicates that $C_{60}$ molecules are mainly incorporated on the dangling bonds of Ga atoms due to the high binding energy between $C_{60}$ molecules and Ga atoms. $C_{60}$ uniformly doped GaAs layers show highly resistive characteristics, suggesting that $C_{60}$ molecules cannot be decomposed into isolated C atoms in the GaAs lattice, and they behave as if they were electron traps or strong recombination centers. C-V profiles of Cr-Au / $C_{60}$ δ-doped GaAs Schottky diode suggest that $C_{60}$ molecules in GaAs lattice produce electron traps which can be charged or discharged by applied electrical field.

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**Keywords**: A1. Doping; A1. Reflection high energy electron diffraction; A1. Capacitance; A3. Molecular Beam Epitaxy; B1. Fullerenes; B2. Semiconducting gallium arsenide

## 1. Introduction

$C_{60}$ molecules are highly symmetric and crystallize into a face-centered cubic (fcc) structure on crystalline substrates such as Si and GaAs [1-5]. However, $C_{60}$ crystals are very fragile and chemically unstable due to the fact that $C_{60}$ crystals are formed by the van der Waals force, which is very weak compared with other bonding structures such as covalent and ionic bindings [6]. Therefore, applying $C_{60}$ crystals to practical devices is very difficult. In contrast, $C_{60}$-doped materials such as $C_{60}$-doped GaAs are quite stable, but only a few reports have been published so far [7].

In the present work, to investigate the crystalline and electrical characteristics of $C_{60}$ doped GaAs layers, we fabricate $C_{60}$ uniformly doped and $\delta$-doped GaAs layers by migration enhanced epitaxy (MEE) method [8]. Reflection high energy electron diffraction (RHHED) and X-ray diffraction (XRD) measurements are used for crystalline characterization of the layers, and Hall-effect measurement and capacitance-voltage (C-V) measurement are adopted for the analysis of their electrical properties. $C_{60}$ uniformly doped GaAs layers show highly resistive characteristics, suggesting that $C_{60}$ molecules cannot be decomposed into isolated C atoms in the GaAs lattice and they behave as if they were electron traps or strong recombination centers. C-V profiles of Cr-Au / $C_{60}$ $\delta$-doped GaAs

Schottky diodes suggest that $C_{60}$ molecules in GaAs lattice produce electron traps which can be charged or discharged by applied electrical field.

## 2. Experimental Procedure

$C_{60}$ uniformly doped and $\delta$-doped GaAs layers are grown on GaAs (001) substrates by using solid source molecular beam epitaxy (MBE) method. GaAs substrates are first etched in an alkaline etchant, and loaded in the growth chamber. Native oxide layers of GaAs surfaces are removed by a thermal flash at 580°C in $As_4$ atmosphere. After growing a 100nm-thick GaAs buffer layer at 580°C, $C_{60}$ doped GaAs layer growth is performed at a substrate temperature of 300°C. The growth rate of GaAs is fixed at 0.5 monolayer/s (ML/s). The MEE deposition sequence (1 cycle) consist of 2s Ga supply and 2s $As_4$ supply. 99.5% $C_{60}$ powder is used as the $C_{60}$ source. The beam equivalent pressure (BEP) of $C_{60}$ is varied between $1.0 \times 10^{-8}$ Torr and $1.0 \times 10^{-7}$ Torr. $C_{60}$ deposition is performed during Ga deposition period because the sticking coefficient of $C_{60}$ molecules on Ga surface is higher than that on As surface [7]. RHEED patterns are monitored during the layer growth. The crystalline properties are investigated by XRD pole-figure measurements. The electrical properties are investigated by Hall-effect measurement.

## 3. Results and Discussion

Characterizations by TEM and SIMS measurements show that $C_{60}$ uniformly doped

GaAs layers with no segregation and well-defined δ-doped structures are constructed by MEE methods [7]. No 2D defect is confirmed for $C_{60}$ uniformly doped GaAs layers with the carbon concentration below $1.0x10^{20}cm^{-3}$ and $C_{60}$ δ-doped GaAs layers with the carbon doping density below $5.0x10^{14}cm^{-2}$. However, 2D defects are found in the grown layers when the $C_{60}$ concentration is much higher than these values.

We discuss the 2D defects induced by $C_{60}$ high-concentration doping. Fig. 1 shows RHEED patterns of a 50ML thick $C_{60}$ uniformly doped GaAs layer with the carbon concentration of $5x10^{20}cm^{-3}$ grown at 300°C. Electron beam azimuth is along [110] (Fig. 1a) and [-110] (Fig. 1b) directions. RHEED patterns show (1x1) streak structures when the carbon concentration is below $1.0x10^{20}cm^{-3}$. In contrast, Fig. 1a shows clear chevrons patterns which are refracted along <111> directions, suggesting that {111}B facets are formed on the surface. The pattern shown in Fig. 1b is obtained when the beam azimuth is along [-110] direction. This diffraction pattern is very complex, but can be explained by the rotational domains. The diffraction pattern model is shown in Fig. 1b. The black circles are the diffraction spots from the epitaxial GaAs layer oriented to [001] direction. While, the gray circles show inverted diffraction spots along [-1-11] axis caused by rotational domains on (-1-11)A plane. The white circles are the inverted diffraction spots along [111] axis induced by rotational domains on (111)A plane as with the gray circles. Then, RHEED diffraction pattern in Fig. 1b is composed with the black diffraction spots and superimposed spots from rotational domains as with the results of other material with twin formations [9-11].

To investigate the rotational domains, XRD pole-figure measurements are performed. Fig. 2 shows pole-figures of a $C_{60}$ uniformly doped GaAs layer with the carbon concentration of $5x10^{20}cm^{-3}$ where $2\theta$ is set to 27.3° [GaAs (111) diffraction]. For single crystalline GaAs (001) substrates, only four diffraction peaks at $\psi$=54° [111, 1-11, -1-11, -111] are detected shown in Fig. 2a. However, many diffraction peaks from the $C_{60}$-doped GaAs layer are confirmed in the figures. Fig. 3 shows a GaAs crystal structure with a rotational domain on (111)A plane. This domain is rotated by 180° about [111] axis and this dislocation type is twin faults. Diffraction peaks surrounded by dotted-lines in Fig. 2a are induced from the domain with twin faults on the (111)A plane. The highlight peaks in Fig. 2b are induced from the domain with twin faults on the (-111)B plane. The other new diffraction peaks are also explained by the model of twin formations as with the results of other materials [12, 13].

These pole-figure patterns show that the rotational domains appear mainly on the {111}A plane. This result coincides with the result of RHEED observations. The twin faults formation suggests that $C_{60}$ adsorption tends to occur on the dangling bonds from Ga atoms due to the high binding energy between $C_{60}$ molecules and Ga atoms. Therefore, the twin faults appear predominantly on {111}A plane compared with {111}B plane.

Next, we discuss the electrical properties of $C_{60}$ $\delta$-doped GaAs layers. Coulomb blockade phenomenon using $C_{60}$ molecules in $SiO_2$ layers are reported [14]. This result suggests that $C_{60}$ molecules in other materials keep their molecular structure and are active in electrical properties of the devices. All the $C_{60}$ uniformly doped GaAs layers are confirmed to show highly resistive characteristics, and Si-$C_{60}$ co-doped GaAs layers show n-type conductivity when the doping level of Si is beyond that of carbon. These results are explained by the model that $C_{60}$ molecules cannot be decomposed into isolated C atoms in the GaAs lattice and they behave as if they were electrons traps or strong recombination centers [7]. To investigate the behavior of $C_{60}$ molecules more precisely, C-V measurements of $C_{60}$ $\delta$-doped GaAs layer are performed. Fig. 4 shows a sample structure of Cr-Au / $C_{60}$ $\delta$-doped GaAs Schottky diodes grown on n-type GaAs (001) substrates. After removing a native oxide layer on the substrate surface, 1$\mu$m-thick n-type GaAs layer with Si concentration of $1x10^{16}cm^{-3}$ is grown at 580°C by MBE. After that, the substrate temperature is lowered to 400°C, and $C_{60}$ $\delta$-doping is performed. The $C_{60}$ density used for the $\delta$-doping is far below the “2D defect formation” level. In this study, the $C_{60}$ BEP is $1.0x10^{-7}$ Torr and the $C_{60}$ shutter opening time is 30s. With this condition, the $C_{60}$ density of the $\delta$-layer is estimated to be approximately $2x10^{12}cm^{-2}$. After 10ML-thick GaAs capping layer growth by MEE, 1$\mu$m-thick GaAs layer with same Si concentration is deposited at 580°C. A sample with the same structure except $C_{60}$ $\delta$-doping is also fabricated for comparison by closing the $C_{60}$ cell shutter during growth. Cr-Au contact is evaporated on these samples.

Fig. 5 shows $1/C^2$ versus voltage profiles of Cr-Au / $C_{60}$ $\delta$-doped GaAs Schottky diodes and the energy band profile of the Schottky diode in the bias voltage between -3V and -25V. The lateral axis of the $1/C^2$ versus voltage profiles denotes applied reverse-bias voltage. The black points mean the results of the $C_{60}$ δ-doped GaAs sample, and the gray points show the results of the sample grown under the $C_{60}$-shutter-close condition. When the bias voltage is 0V, the depletion layer edge is located at 300nm below the rectifying contact. At -3V bias voltage, the depletion layer edge reaches the $C_{60}$ δ-doping layer, and the capacitance keeps same value until the applied voltage reaches -25V. This indicates that the density of electron traps is approximately $1.5x10^{12}cm^{-2}$. For the sample grown under the $C_{60}$-shutter-close condition, the trap concentration is estimated to be $5.7x10^{11}cm^{-2}$. In the latter, $C_{60}$ is probably supplied from the background. These results suggest that $C_{60}$ molecules in GaAs produce electron traps which can be discharged by applied electrical field. The energy band profiles in Fig. 5 shows the model that the trapping centers induced by $C_{60}$ doping release electrons by applied electrical field.

**4. Conclusions**

$C_{60}$ uniformly doped GaAs layers with no segregation and well-defined δ-doped layers are successfully fabricated by MEE method. $C_{60}$ high-concentration doping is found to introduce 2D defects. RHEED and XRD pole-figure measurements show that the twin faults occur predominantly on {111}A plane, indicating that $C_{60}$ molecules are mainly incorporated on the dangling bonds from Ga atoms due to high binding energy between $C_{60}$ molecules and Ga atoms. $C_{60}$ uniformly doped GaAs layers show semi-insulating characteristics, suggesting that $C_{60}$ molecules may keep their molecular structures in the GaAs lattice, and they behave as if they were electron traps or strong recombination centers. C-V profiles of Cr-Au / $C_{60}$ $\delta$-doped GaAs Schottky diodes suggest that $C_{60}$ molecules in GaAs lattice produce electron traps which can be charged or discharged by applied electrical field.

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**Figure captions**

Fig. 1. RHEED patterns of a $C_{60}$-doped GaAs layer with carbon concentration of $5x10^{20}$ $cm^{-3}$ grown at 300°C. Electron beam azimuth is [110] azimuth (Fig. 1a) and [-110] azimuth (Fig. 1b).

Fig. 2. XRD pole-figures of a 200nm thick $C_{60}$-doped GaAs with carbon concentration of $5x10^{20}$ $cm^{-3}$ where $2\theta$ is set to 27.3° [GaAs (111) diffraction].

Fig. 3. A model of GaAs (001) surface with a rotational domain induced by twin faults. The domain is rotated by 180° about the [111] direction on the (111)A plane.

Fig. 4. Cr-Au / $C_{60}$ $\delta$-doped GaAs Schottky diode structure grown on n-type GaAs (001) substrate.

Fig. 5. $1/C^2$ versus voltage profiles for Cr-Au / $C_{60}$ $\delta$-doped GaAs Schottky diodes and the energy band profile of the Schottky diode in the bias voltage between -3V and -25V. The black points mean the results of the $C_{60}$ $\delta$-doped GaAs sample, and the gray points shows the results of the sample grown under the $C_{60}$-shutter-close condition.

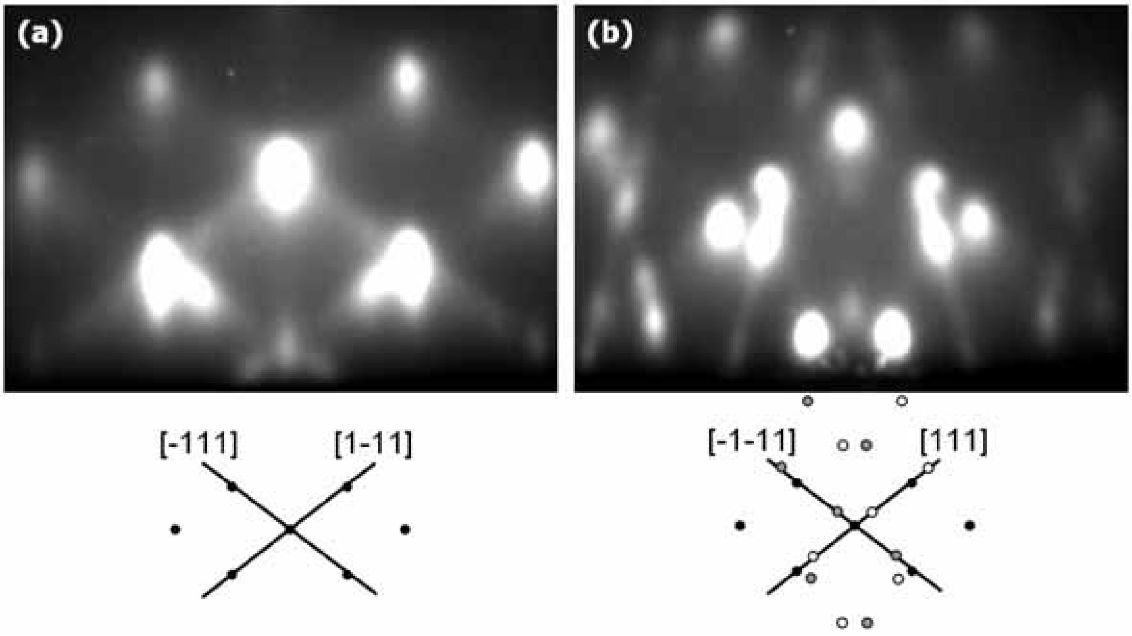



Fig. 1

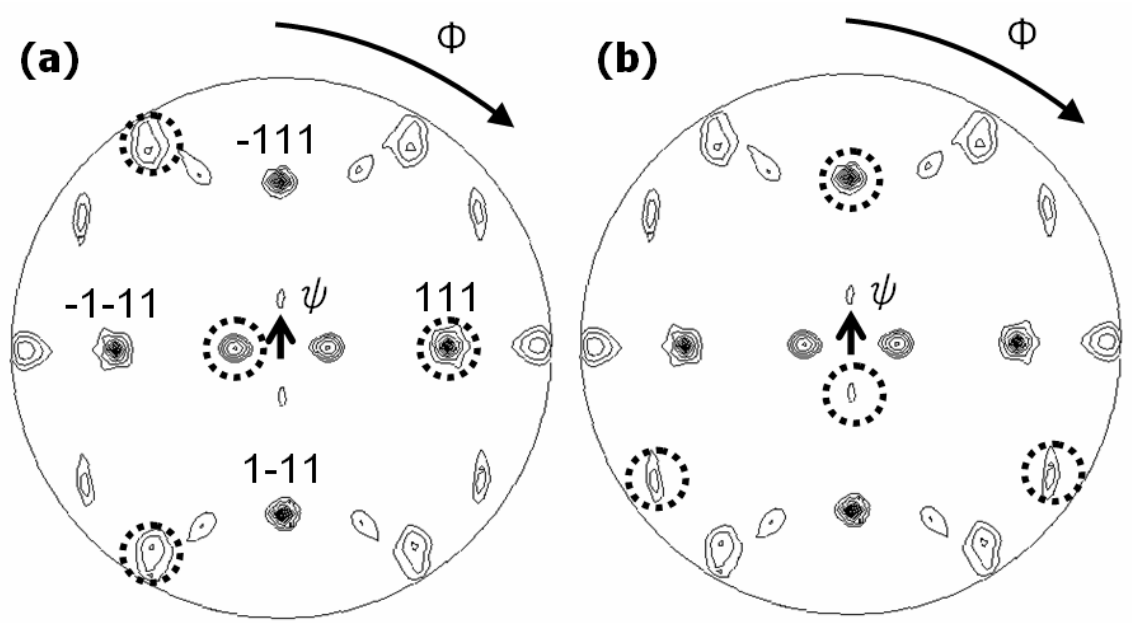



Fig. 2

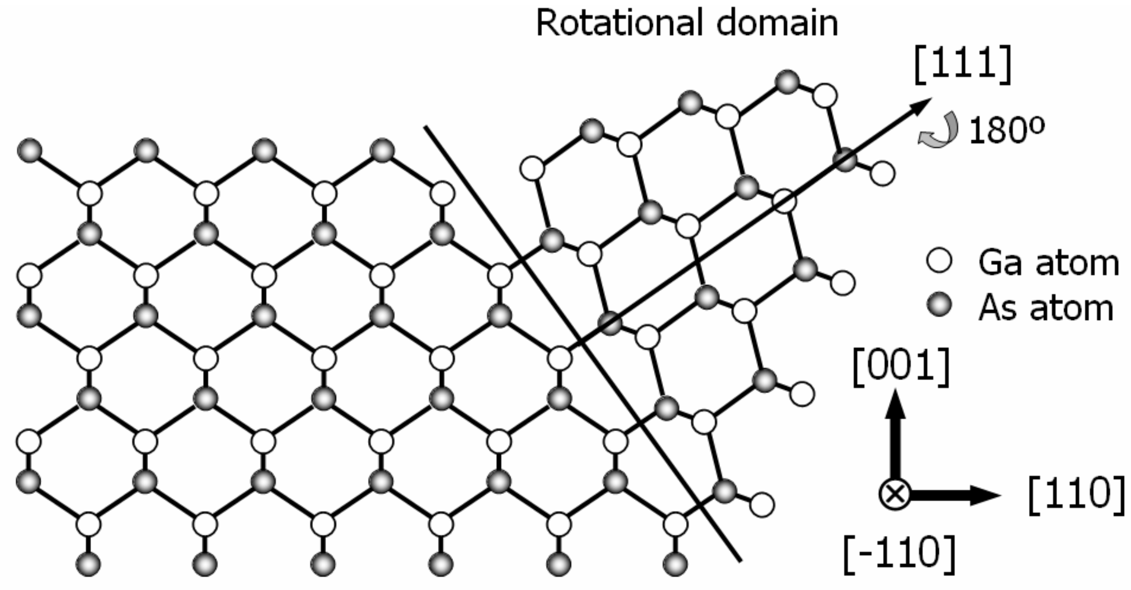

Rotational domain
[111]
180°
Ga atom
As atom
[001]
[110]
[-110]

Fig. 3

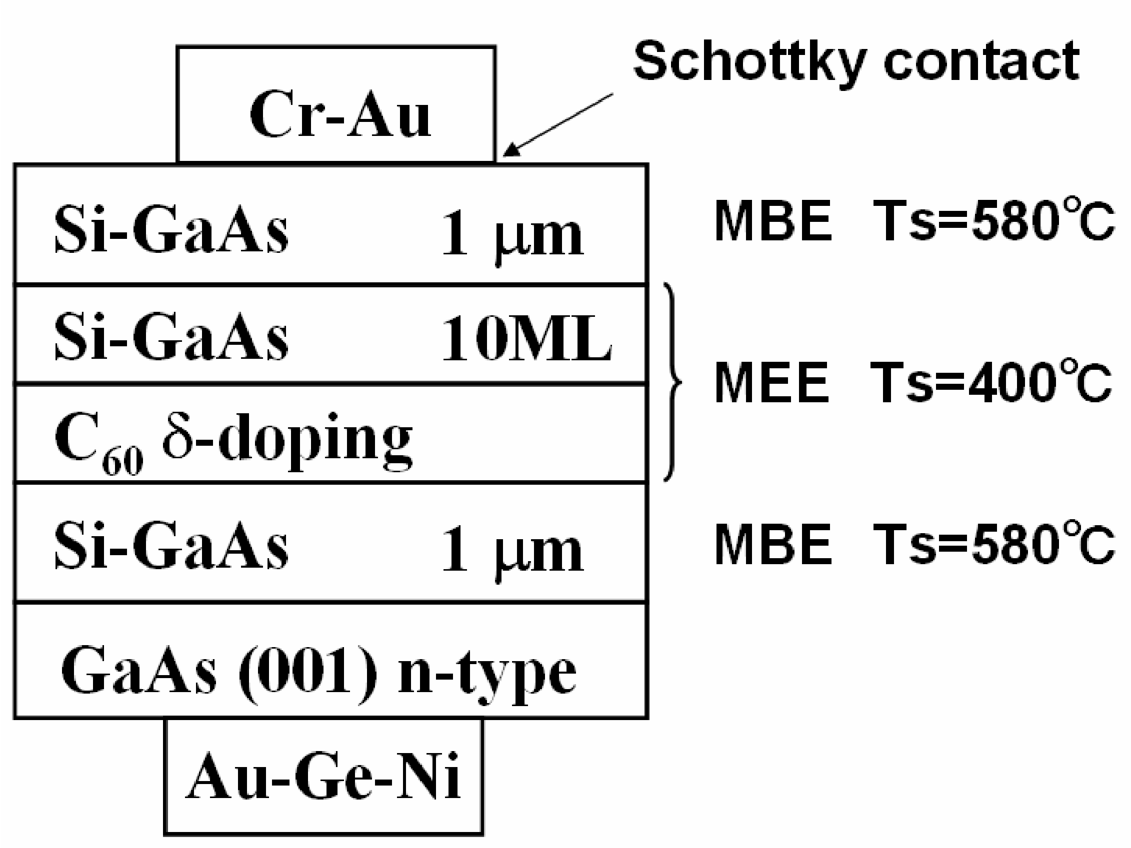
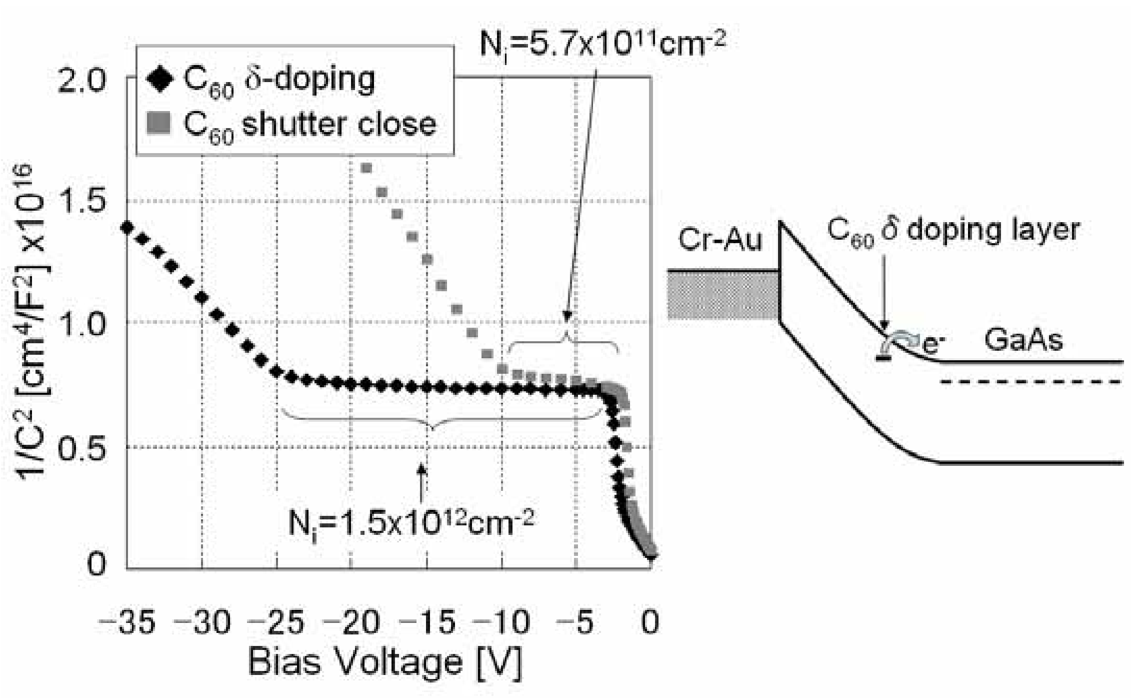

Schottky contact
Cr-Au
Si-GaAs 1 μm
MBE Ts=580℃
Si-GaAs 10ML
C60 δ-doping
MEE Ts=400℃
Si-GaAs 1 μm
MBE Ts=580℃
GaAs (001) n-type
Au-Ge-Ni

Fig. 4



C60 δ-doping
C60 shutter close
Ni=5.7x10¹¹cm⁻²
Ni=1.5x10¹²cm⁻²
1/C² [cm⁴/F²] x10¹⁶
2.0
1.5
1.0
0.5
0
−35 −30 −25 −20 −15 −10 −5 0
Bias Voltage [V]
Cr-Au
C60 δ doping layer
e⁻
GaAs


Fig. 5