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Dynamics of surface photo-voltage in GaAs systems studied with time-resolved photoelectron spectroscopy

时间分辨光电子能谱下砷化镓系统表面光电压动力学

Masao Kamada[1*], Junpei Azuma[1], Senku Tanaka[2] and Kazutoshi Takahashi[1]

[1]*Synchrotron Light Application Center, Saga University, Saga 840-8502, Japan*
[2]*Department of Electric and Electronic Engineering, Faculty of Science and Engineering, Kinki University, Higashiosaka 577-8502, Japan*

kamada@cc.saga-u.ac.jp

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Abstract - **Experimental data of Surface Photo-Voltage (SPV) on GaAs(100) are presented, which were obtained with time-resolved photoelectron spectroscopy using synchrotron radiation and laser light or ultra-fast laser lights. Clean p- and n-type GaAs with different dopant concentrations were measured at room and low temperatures. The experimental results of the static SPV can be well explained by a thermionic model. On the other hand, the results of the dynamic SPV show clearly the creation and annihilation processes, where the temporal structures of SPV involve slow and fast components. The fast component indicates the important role of hot carriers and non-thermionic process, while the slow one is attributed to the thermionic process. Finally, two ideas for suppressing the SPV effect have been examined to get a higher performance of solar cells and electron emitters.**

Keywords - **Surface Photo-Voltage, Time-resolved photoelectron spectroscopy, Dynamics, GaAs, Non-thermionic process**

I. INTRODUCTION

Solar cells are indispensable devices to generate electric power from natural lights. The key idea originates from a Photo Voltage (PV) effect of semiconductors [1]. Further understandings of the PV mechanism are required to get more efficient, intelligent and cheap solar cells. Moreover, deep understandings of Surface Photo-Voltage (SPV) are required in Schottky-type solar cells and in the field of high-energy accelerator to produce a high-brilliant and ultra-short beam using a photo-cathode [2]. Moreover, the spin electrons attract recent interest for a spin solar cell [3]. These applications need different technologies, internal and external photoelectric effects in semiconductors and interfaces, but the essential point shares common basic understandings. The concepts of band bending and static SPV are based on the electromagnetic theory and a thermionic emission model. In the pn-junction type solar cells, photo-excited electrons and holes are spatially separated by the internal field caused in the pn junction as well as by the thermal diffusion. Separated electrons and holes produce a reverse electric field. In Schottky-type solar cells, photo-excited electrons and holes are spatially separated by the internal field originated from the interface between metal and semiconductors and also produce a reverse electric field. These reverse electric fields affect the performance of solar cells.

On the other hand, it is essential in the electron sources that photo-excited electrons overcome the surface barrier with the lowest excitation photon energy. The key factors are the large band bending and the low or negative electron affinity. For high brilliant excitation, however, photo-electric yields show saturation or decrease due to the SPV effect: Photo-excited electrons and holes are spatially separated to produce photo currents and a reverse electric field, which affects the performance of electron sources. Therefore, it is important to suppress the SPV effects to improve the efficiency of electron sources as well as solar cells.

Firstly in this report, the present authors introduce their experimental works of SPV on p- and n-type GaAs, which have been obtained with a combinational use of synchrotron radiation (SR) and laser light [4-6]. The differences in static SPV between p- and n-types are explained with a thermionic model. Secondly, dynamics of SPV measured with a time-resolved photoelectron spectroscopy and ultra-fast laser lights are introduced [7-9]. The present results show clearly the creation and annihilation processes of SPV, where temporal structures of SPV involve slow and fast components. The fast component indicates the important role of hot carriers and non-thermionic process, *i.e.* non-equilibrium dynamics, while the slow one is attributed to the thermionic process. Finally, two ideas for suppressing the

SPV effect have been examined in order to get higher performance of solar cells and electron emitters.

II. EXPERIMENTS

The experiments were carried out at UVSOR BL5A & 6A2 in Institute for Molecular Science and Saga-University BL13 in Saga-LS. Combined systems of SR and laser light with the photoelectron spectroscopy were applied to study SPV effects. As shown in the schematic diagram of the experiments (Fig. 1), sample surfaces were excited with laser light (*523 nm* or *800 nm*) to produce excited electrons and holes. Photoelectrons from a sample core-level were observed using monochromatized SR and hemi-spherical photoelectron spectrometers.

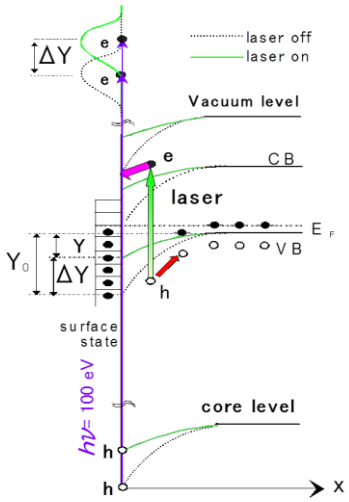

Fig. 1. A schematic diagram of the experiments [5]. Y_0, and ΔY are initial band bending and SPV, respectively. e and h mean an electron and a hole, respectively.

This laser-pump and SR-probe core-level photoelectron spectroscopy has high surface sensitivity, high energy resolution and time resolution (typically, in the subnano to micro second region) besides element-specific and state-selective performances. Moreover, ultra-fast temporal data (typically, in the femto to pico second region) were obtained with a laser-pump and laser-probe photoelectron spectroscopy using Ti:Sapphire femto-second laser systems. The details of the experimental systems have been reported elsewhere [5-6, 10-11], and a typical system is also shown in Fig. 2.

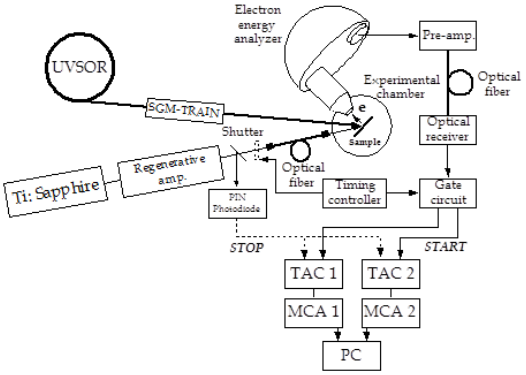

Fig. 2. An experimental system for time-resolved photoelectron spectroscopy [6].

Clean p- and n-type GaAs(100) with different dopant concentrations were measured at room and low temperatures. To investigate the effects of hole mobility, surface barriers and surface states, GaAsP super-lattices and Cr/GaAs(100) samples were investigated [6,12-13]. Surfaces of GaAs were cleaned with a neon-ion sputtering and a thermal annealing, while super-lattice surfaces were cleaned only with thermal treatments. The surface cleanness was checked with an Auger and/or photoelectron spectroscopy after the cleaning procedures, indicating negligible carbon and oxygen contaminations. Moreover, the GaAs (100) surfaces were checked with a low-energy-electron diffraction, showing the c(8x2) reconstruction.

III. RESULTS and DISCUSSION

3-1. Thermionic model

Semiconductor surfaces show a band bending, which depends on the surface states and dopant concentration. Photoexcited carriers are spatially separated by the internal electric field in the band bending region and by the thermal diffusion. The separated carriers produce SPV as well as photo-currents. In a thermionic model, photo-carriers are assumed to be in the thermal distribution. The dotted curves in Fig. 3 show valence band maximum (VBM) and conduction band minimum (CBM) in the surface region of a p-type semiconductor, which contacts with metallic surface layer, producing a Schottky-type interface. They show the band bending without photoexcitation. The SPV changes the potential in the surface region, which is shown by a solid curve. After approximation procedures in the thermionic model, we can obtain the following Equation (1) [5], where p_0 and δp are initial concentration and increment of positive carriers, respectively, and β, ψ_0 and $\Delta\psi$ are $1/kT$, initial band bending and SPV, respectively.

$$\ln\{\beta\Delta\psi\cdot\exp(\beta\Delta\psi)\}\approx\ln\left(\frac{\delta p}{p_0}\right)+\beta\psi_0 \qquad (1)$$

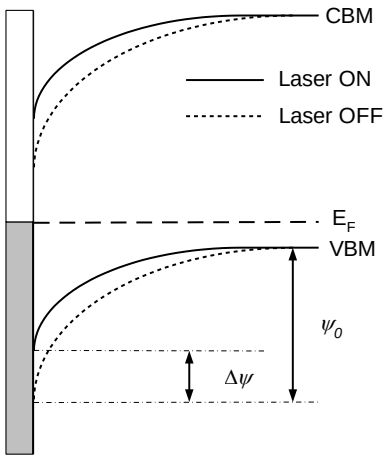

Fig. 3. Band bending and SPV.

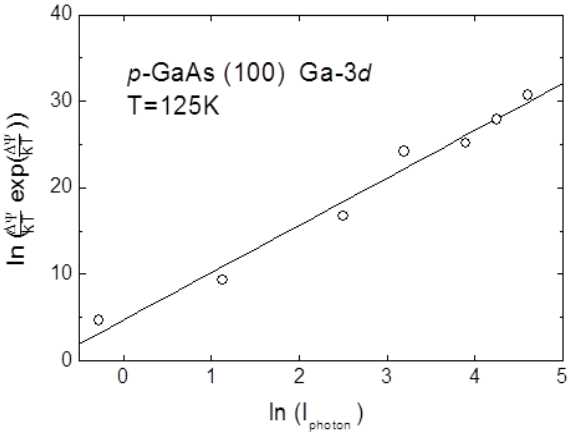

Fig. 5. Comparison of the observed SPV and theoretical line (Eq. (1)) based on a thermionic model [5].

3-2. Photon flux dependence of SPV

Figure 4 shows the energy shift of Ga-3d photoelectrons of p-GaAs at 125 K (open circles) as a function of relative incident photon flux. The shift is caused by the SPV under the laser irradiation at 2.33 eV. It is seen that the amount of SPV increases rapidly for low fluxes and gradually increases for middle fluxes, and saturates for higher fluxes. This experimental result is well explained with Eq. (1) mentioned above. Figure 5 shows the comparison of the present result with Eq. (1), where the ordinate and abscissa are presented in natural logarithms according to Eq. (1). The linear solid line and open circles are the theoretical curve and experimental data, respectively. The observed data are in good agreement with the theoretical line from Eq. (1) [5].

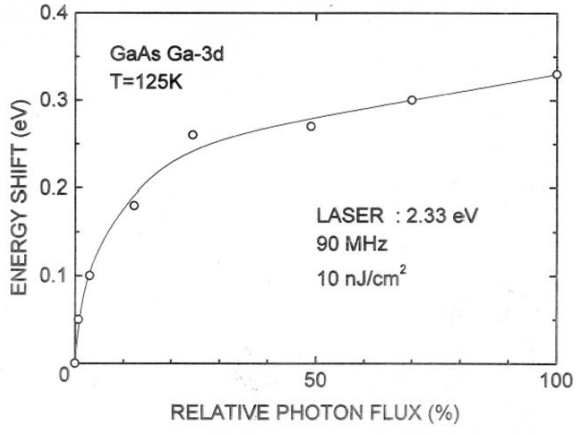

Fig. 4. Energy shift of Ga-3d photoelectrons as a function of incident photon flux.

3-3. Temperature dependence of SPV

As Eq. (1) is derived from a thermionic model based on the thermal equilibrium, the temperature dependence of SPV is very important and essential examination for the thermionic model. Figure 6 shows the temperature dependences of SPV on p- and n-GaAs (100) surfaces. As the direction of the energy shift of the Ga-3d photoelectrons is opposite between p- and n-GaAs, the absolute values of the energy shift (SPV) are plotted in Fig. 6 as a function of the sample temperature. It is seen that the temperature dependence of SPV is opposite between p- and n-GaAs; *i.e.* the amount of SPV increases in p-GaAs but decreases in n-GaAs as the sample temperature is increased. This difference in the temperature dependence can be explained with the thermionic model as follows. Figure 7 shows the temperature dependence of SPV on p-GaAs, where

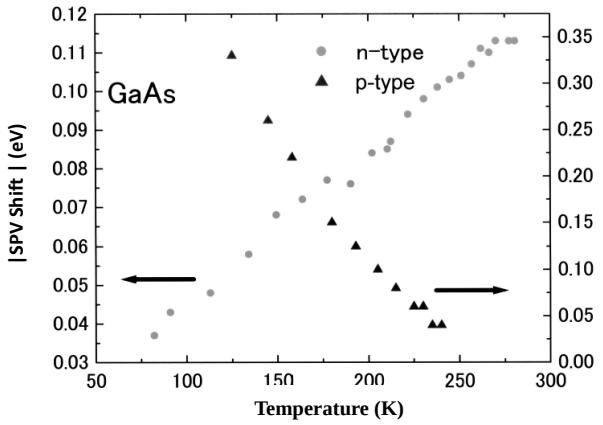

Fig. 6. Temperature dependences of SPV on n-GaAs (solid circle) and p-GaAs (solid triangle). The absolute values are shown for comparison, since the direction of energy shift due to the SPV effect is opposite between p- and n-GaAs.

the ordinate and abscissa are presented according to Eq. (1) [5].

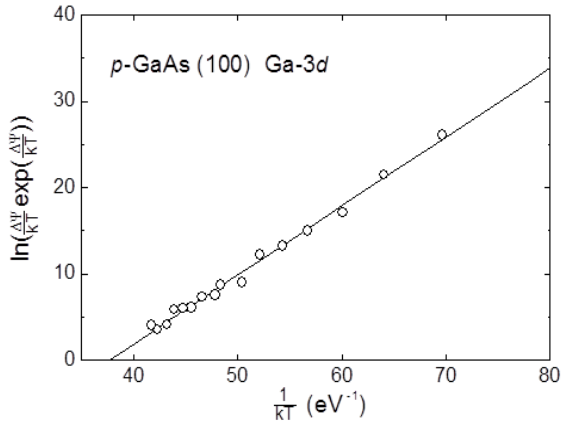

Fig. 7. Temperature dependence of SPV on p-GaAs. The linear line presented according to Eq. (1) fits well the observed data points [5].

The temperature dependence of ψ_0 in Eq. (1) is not clearly described above, but ψ_0 is in general dependent on temperature, since it is determined in the thermal equilibrium between dopant concentration and surface states. The quantity can be observed as the band offset, and the experimental results show that the band bending is

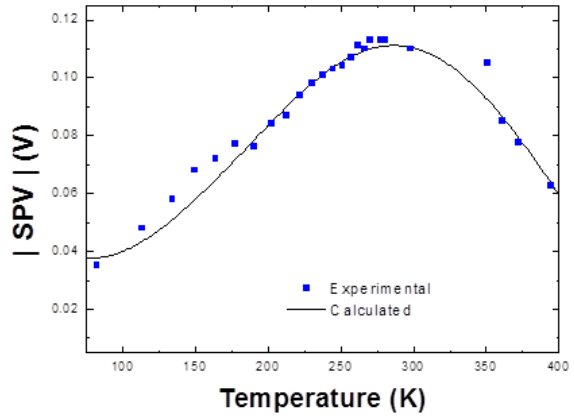

Fig. 8. Temperature dependence of SPV on n-GaAs. The calculated curve includes the temperature dependence of the band bending.

almost temperature independent for p-GaAs, but increases for n-GaAs as the temperature is increased. By taking account of the temperature dependence of $\psi_0(T)$ and using Eq. (1), the SPV on n-GaAs can be explained, as shown in Fig. 8. Therefore, it is concluded that the temperature dependence of SPV on both p- and n-GaAs is well understood with Eq. (1) based on the thermionic model, and the difference between p- and n-GaAs is attributed mainly to the temperature dependence of the band bending.

3-4. Dynamics of SPV

Photoexcited carriers produce photo current and SPV, and the carriers decay to the initial stage. We have carried out the time-resolved experiment to know the dynamics of SPV. The SPV processes are schematically shown in Fig. 9. That is, (a) excited carriers are produced by photo excitation, and subsequently (b) photocarriers are spatially separated to produce photo current and SPV, and (c) the carriers overcome the surface potential barrier and recombine with each other to go back to the initial stage before photoexcitation.

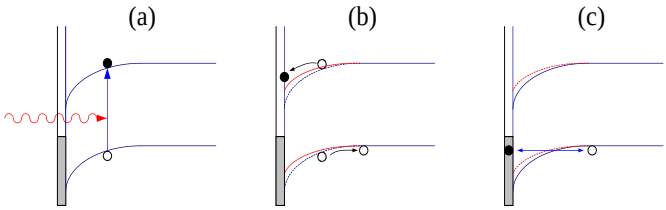

Fig. 9. Three processes of SPV. (a) photoexcitation, (b) creation, and (c) annihilation.

Figure 10 shows the temporal structures of SPV on p-GaAs at room temperature (RT) and 90 K. At RT, the SPV is created and then annihilated in a short period of about *0.5* μs, while at 80 K, the SPV decays with a fast component of about *5* μs and a slow component accumulated as the background. The slow component is not seen at RT. The present results indicate that a part of SPV is caused by thermal process, while another part is due to non-thermal process [6]. It is supposed that the observed temporal structures are mainly determined by the decay process (c) in Fig. 9.

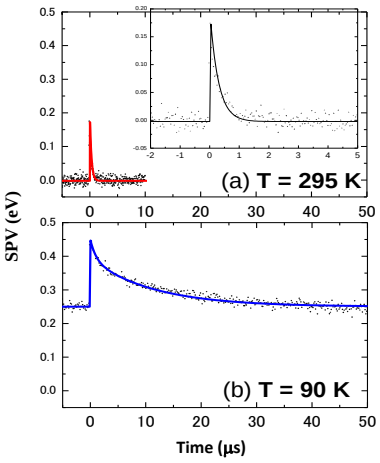

Fig. 10. Temporal structures of SPV at RT and 80 K [6].

3-5. Ultra-fast dynamics of SPV

We have measured the ultra-fast time-resolved photoelectron spectra using a laser-pump and laser-probe method. The results show the ultra-fast creation and annihilation processes of SPV. As seen in Fig. 11(a) [8], the

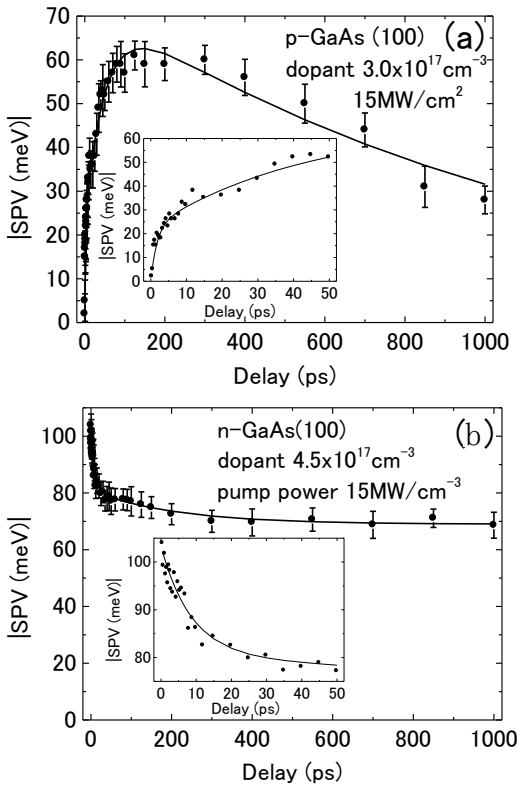

Fig. 11. Ultra-fast temporal structures of SPV. (a) p-GaAs and (b) n-GaAs.

creation process of SPV on p-GaAs has the rise time in pico-second region. The rise time is dependent on dopant concentration: The rise time becomes very fast in case of high dose samples, but it does not clearly show the temperature dependence. On the other hand, the rise process is not observed in Fig. 11(b) for n-GaAs [7], which has the high electron mobility. Therefore, the rise time observed on p-GaAs is attributed to the drift velocity v which is originated from hole mobility μ and inner electric field E in the band bending region. As seen in Fig. 11(a) and 11(b), the decay time of SPV consists of an ultra-fast and a slow component for both p- and n-GaAs, and the ultra-fast component is independent on the sample temperature, but the slow one has strong temperature dependence and dopant-concentration dependence as well. This result indicates that the decay process of SPV is caused by thermal and non-thermal processes and the ultra-fast component is due to the tunneling process and the slow component is due to the thermionic or thermionic+ tunneling process. Moreover, the total amounts of SPV on n-GaAs depend on excitation density, but the ultra-fast decay component is independent on excitation density. As seen in Fig. 12, the amount and lifetime of the ultra-fast component is almost fixed. (*e.g.* the lifetime is about *5 ps*). Therefore, lifetime of ultra-fast component is due to relaxation time of hot electrons

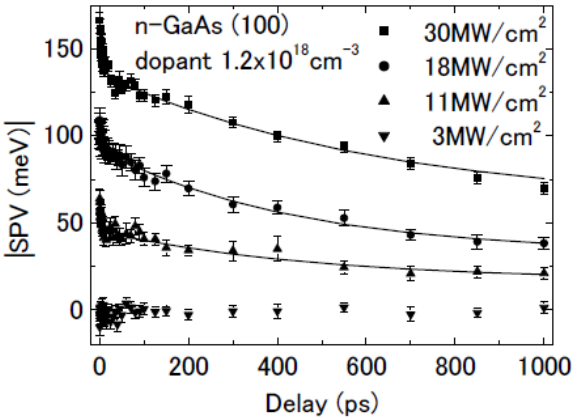

Fig. 12. Excitation density dependence of SPV on n-GaAs in the ultra-fast region.

3-6. Two ideas to suppress SPV

High brilliant photon excitation causes the saturation or decrease in solar cells or electron emitters. As mentioned above, one of the main reasons to cause such effects is the SPV, and it is therefore important to suppress SPV in order to have high performance of solar cells or electron emitters. There are two ideas proposed previously [14,15]. One is to control the spatial separation of holes using quantum wells [14]. This is also useful to get high degree of spin polarization for the electron source. Another is to increase recovery force using metallic surface layers [15]. Both ideas were examined by the laser-pump and SR-probe photoelectron spectroscopy and the results were partially

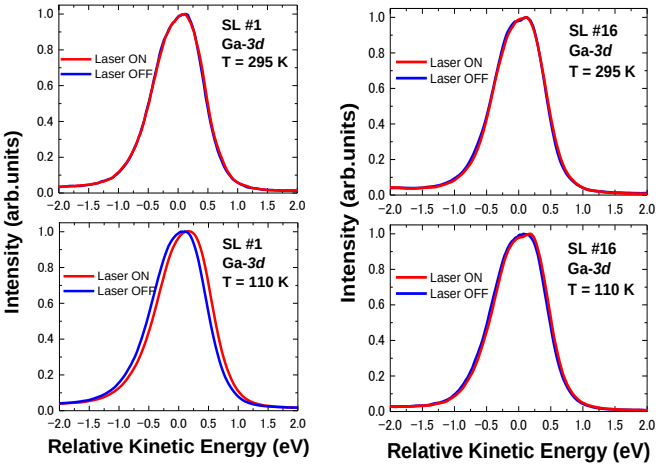

Fig. 13. Ga-3d photoelectron spectra of two super-lattices (SL#1 and SL#16) with and without laser excitations at RT and 110 K.

reported elsewhere [6,13], and the essential points are given in the followings. Figure 13 shows the Ga-3d photoelectron spectra with and without laser excitations on two-types super-lattices (SL#1 and SL#16) at RT and 110K, where the large space charge region of SL#1 and SL#16 is *4* and *34 nm*,

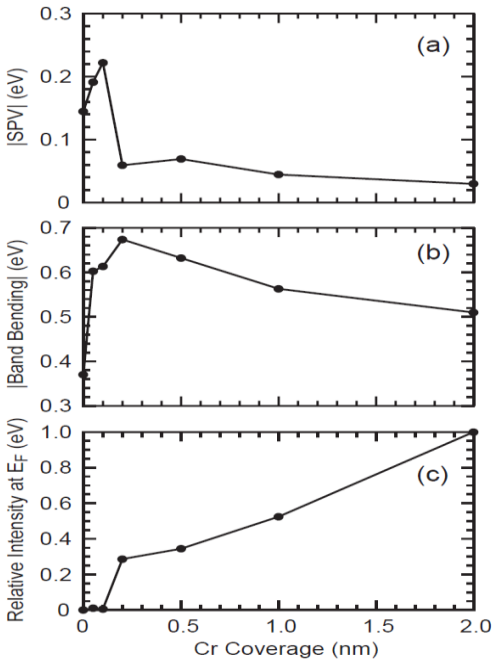

Fig. 14. SPV, band bending, and density of states around Fermi energy of Cr/GaAs as a function of Cr coverage.

respectively. Both spectra observed at RT do not show any SPV and those at 110 K show slight SPV shift. Their temporal structures also indicate negligible SPV at RT and small sharp peak for SL#1, but not for SL#16 [6]. The results mean that the control of the hole transfer in quantum well as well as the thin space charge region are effective to suppress SPV. Figure 14 shows SPV, band bending and density of states around Fermi energy of Cr/GaAs as a function of Cr coverage. The SPV value has a maximum around *0.1 nm* of Cr overlayer and decreases as a function of Cr coverage. The decrease of SPV is seemed to relate with the density of states around Fermi energy. It is suggested from the results that the recombination, or quick recovery in the surface region is important to suppress SPV.

III. SUMMARY

The SPV on p- and n-type GaAs, which have been obtained with a combinational use of synchrotron radiation and laser light, has been reported. The differences in static SPV between p- and n-types are explained with a thermionic model. Dynamic SPV data obtained with a time-resolved photoelectron spectroscopy and ultra-fast laser lights are discussed. The present results show clearly the creation and annihilation processes of SPV, and the temporal structures of SPV consist of slow and fast components. The fast component indicates the important role of hot carriers and non-thermionic process, *i.e.* non-equilibrium dynamics, while the slow one is attributed to the thermionic process. Two ideas for suppressing the SPV effect have been examined in order to get higher performance of solar cells and electron emitters.

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