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The authors report on the electrical and photoconductivity characteristics of donor-acceptor alternating copolymer, poly(dioctyloxinapthalenediketopyrrolopyrrole) (PONDPP) with Al/PONDPP/p-Si/Al hybrid organic/inorganic Schottky diode for optoelectronic applications. The fabricated device shows ideality factor value of 2.6 and barrier height of 0.68 eV obtained from current-voltage characteristics. The high rectification ratio of 1.86×10^4 and photo-responsivity of 55 mA/W at 650 nm is achieved. From results, we found that the fine photo-response and electrical characteristics are attributed to the modified band-gap structure to have Schottky barrier at highest occupied molecular orbital to valence band of silicon and high hole mobility of PONDPP.

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The authors report on the electrical and photoconductivity characteristics of donor-acceptor alternating copolymer, poly(dioctyloxinapthalenediketopyrrolopyrrole) (PONDPP) with Al/PONDPP/p-Si/Al hybrid organic/inorganic Schottky diode for optoelectronic applications. The fabricated device shows ideality factor value of 2.6 and barrier height of 0.68 eV obtained from current-voltage characteristics. The high rectification ratio of 1.86×10^4 and photo-responsivity of 55 mA/W at 650 nm is achieved. From results, we found that the fine photo-response and electrical characteristics are attributed to the modified band-gap structure to have Schottky barrier at highest occupied molecular orbital to valence band of silicon and high hole mobility of PONDPP. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4770074]

Research on solution-based organic materials and devices have attracted much attention for the inexpensive organic optoelectronics such as organic light emitting diode (OLED), photo voltaic, optical memory, and phototransistors.[1–4] The advantages of organic materials that have facile band-gap engineering using chemical synthesis and conjugated polymer enable the various properties for photo-conversion devices.[5,6] The band-offset among organic layers is critical issue to improve the optical device performance. The recombination rate of the excited electron and hole on the interface states between various junctions of optical devices strongly depends on the band structure.[7–9] In recent years, considerable approach has been devoted to the organic heterojunction structure or organic-inorganic hybrid junctions due to the large band-offset and their low-temperature processing.[10–13] The category of heterojunctions given on the basis of the work function of the constituent materials has much potential to improve the device structure and new functions adopting various organic materials. The organic-silicon hybrid junction structure, in particular, exploits the advantageous properties of both organic and silicon for low-cost process. Also, the band structure of the organic-silicon has rectifying contact behavior and photoelectric characteristics using photoconductive polymer.[14,15]

In this paper, we developed the hybrid organic-silicon devices using donor-acceptor alternating copolymer, poly(dioctyloxinapthalenediketopyrrolopyrrole) (PONDPP), as the p-type organic semiconductor having hole accumulation/depletion junction with p-type silicon. The introduction of polymer as organic semiconductor is expected to have enhanced thin film stability compared to small organic semiconductor. Moreover, donor-acceptor alternating structured PONDPP has high hole mobility around 0.324 $cm^2\ V^{-1}\ s^{-1}$ as well as low band-gap of 1.36 eV.[16] The low band-gap is favorable for the photon harvesting in the wide range of the light, and the wider band-gap of PONDPP than p-Si is proper to form the Schottky barrier device. We consider the annealing temperature effect on rectifying behavior to improve the electrical properties of devices because the tailoring organic-inorganic heterojunction interface depends on the annealing process. Then, the photoconductive characteristics are investigated through the light illumination system with various wavelength and light power. This work using donor-acceptor alternating copolymer of PONDPP as organic semiconductor via sol-gel process is rarely reported. The investigation of this paper would pave the way of solution-based p-type organic semiconductor for organic photonics.

Polymerization was carried out by well known a palladium catalyzed Suzuki coupling reaction in a nitrogen atmosphere. The polymer was obtained by 3,6-bis (5-bromothiophen-2-yl)-2, 5-bis(2-ethylhexyl)pyrrolo[3,4-c] pyrrole-1,4(2H, 5H)-dione and 2,2′-(1,5-bis(octyloxy)naphthalene-2,6-diyl)bis(4,4,5, 5-tetramethyl-1,3,2-dioxaborolane mmol) with yield of 42%. The polymer was purified by reprecipitation and a flash column with toluene. The structure of polymer was confirmed by H-NMR and IR.[16] The number average molecular weight and polydispersity indexes of the PONDPP were determined with GPC using polystyrene as standard. The Mn of PONDPP was found to be 9.1 kDa with PDI of 1.47. UV-Vis measurements were carried out using UV-Vis-NIR spectrophotometer (Cary 5000: Varian Co. and FR 6500, JASCO CO). Cyclic voltammetry measurements of the polymers were performed using a BAS 100 B/W electrochemical analyzer in acetonitrile with 0.1M Bu_4NClO_4 (tetrabutylammonium perchlorate) as the supporting electrolyte at a scan rate of 100 mV s^{-1}. The potentials were measured against an Ag/AgCl reference electrode with ferrocene as the internal standard. The onset potentials were determined from the intersection of the tangents to the rising current

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and to the background current of the cyclic voltammogram. The film of UV-absorption of PONDPP showed broad absorption in the 300–800 nm with absorption-edge around 923 nm. The energy levels of PONDPP, HOMO, and LUMO were measured by cyclic voltammetry and optical band-gap.

The devices are fabricated on the heavily doped silicon substrate for p-type. As a cleaning process to remove the native oxide layer on the silicon substrate the diluted hydrogen fluoride is used. Then the conventional cleaning process with acetone, methanol, deionized water is implemented in the ultrasonic bath. The metal-semiconductor (MS) contacts for ohmic contact are formed by aluminum evaporation. The powder of PONDPP was dissolved into chloroform with 0.6 wt. %. The PONDPP has been turned out to have good solubility in common organic solvent as well as good thermal stability. Then the solution was mixed on the magnetic stirrer for 6 h and stabilized for overnight. Before the thin film process, the silicon substrate was dried by nitrogen gas blower. After preparation of substrates, the film was coated at 500 rpm for 30 s using spin coater. The post-annealing process was 80 °C, 100 °C for 10 min in air, respectively. The thickness of the film was measured by atomic force microscope (AFM), and the thickness was about 90 nm. The active area of the device was 2.8×10^{-3} cm^2. The current-voltage characteristics of fabricated devices are analyzed using a Keithley model 4200 SCS. The class-a simulator with a 150 W xenon lamp adjusting using a NREL-calibrated mono-Si solar cell, with a KG-2 filter, for and approximately AM 1.5 G1 sun light intensity is used.

The chemical structure of PONDPP, which was alternating copolymer of dialkoxy naphthalene as donor and diketopyrrolopyrrole as acceptor, was shown in Fig. 1(a). The diketopyrrolopyrrole is popular acceptor moieties, which exhibits bright and strong fluorescence with exceptional photochemical and thermal stability.[17] The schematic diagram of device configuration and its equivalent circuit are described in Figs. 1(b) and 1(c). In Figure 2(a), the energy-band diagram of Al/PONDPP/p-Si/Al is depicted. The HOMO and LUMO edge of PONDPP are at 5.25 eV and 3.89 eV, respectively. It is compared to 5.17 eV and 4.05 eV for E_V and E_C of silicon, respectively. The Schottky barrier exists between PONDPP and p-Si. Then, the work function difference causes the upward band-bending of p-Si. According to the Schottky barrier effect, this barrier impedes the hole injection from majority carrier of p-Si into the metal at reverse bias voltage region.[18] Figure 3(a) shows crystal-clear rectified current curve, which indicates that the fabricated device forms Schottky barrier. The reverse saturation current density of 8.6×10^{-6} A/cm^2 at -5 V and the rectification ratio of $I_{\text{foward bias}}/I_{\text{reverse bias}}$ 1.86×10^4 at 10 V are shown in Figure 3(b). The high rectification ratio is due to the hole barrier given by the HOMO-E_V offset and the reasonably high hole mobility of PONDPP. The current voltage characteristics of Schottky contact can be analyzed by the thermionic emission theory (shown in Eqs. (1) and (2)).[19] The V is applied voltage, q is the electronic charge, n is the ideality factor, k is the Boltzmann constant, φ_b is the barrier height, T is the room temperature as measured, R_s is the series resistance, and I_0 is the reverse saturation current. The A is the device active area, A^* is the effective Richardson constant of 32 A/cm^2 k^2 for p-type silicon.[20] According to the Cheung-Cheung method, the series resistance effect for the Schottky diode needs to be considered for its determination.[21] Then, the thermionic emission having the series resistance can be modified as Eqs. (3) and (4)

$$I = I_0 \exp\left(\frac{q(V - IR_S)}{nkT}\right)\left[1 - \exp\left(\frac{-q(V - IR_S)}{kT}\right)\right], \quad (1)$$

$$I_0 = AA^*T^2 \exp\left(\frac{-q(\varphi_b)}{kT}\right), \quad (2)$$

$$I = I_0 \exp\left[\frac{-q(V - IR_S)}{kT}\right], \quad (3)$$

$$\frac{dV}{d(\ln I)} = n\left(\frac{kT}{q}\right) + IR_S. \quad (4)$$

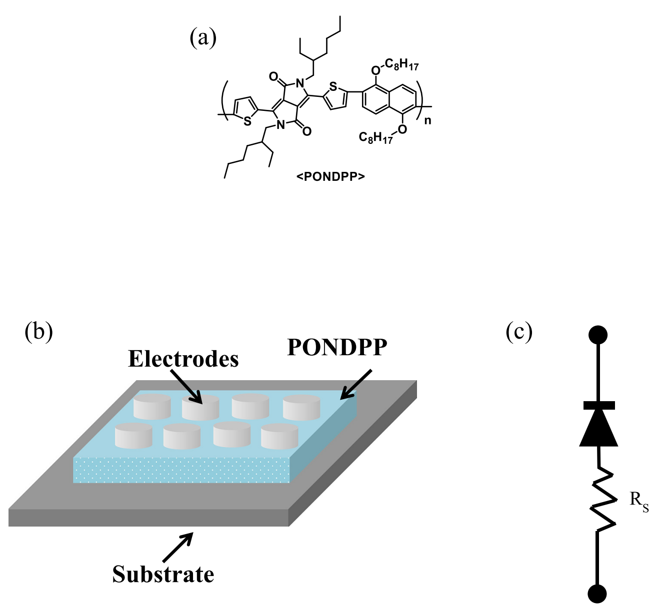

FIG. 1. (a) The molecular structure of PONDPP. (b) The schematic diagram of Al/PONDPP/p-Si/Al structure. (c) The equivalent circuit of fabricated device.

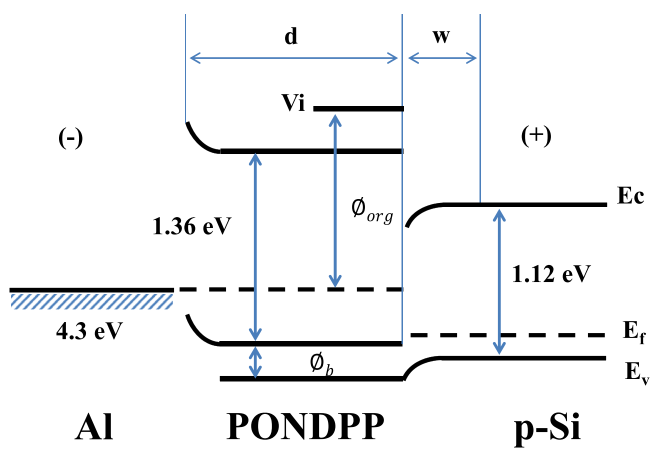

FIG. 2. (a) The energy band diagram for Al/PONDPP/p-Si. The d is the film thickness, φ_b is the barrier height, Vi is the potential drop across the interfacial layer, φ_{org} is the work function of the PONDPP, w is the width of the depletion region.

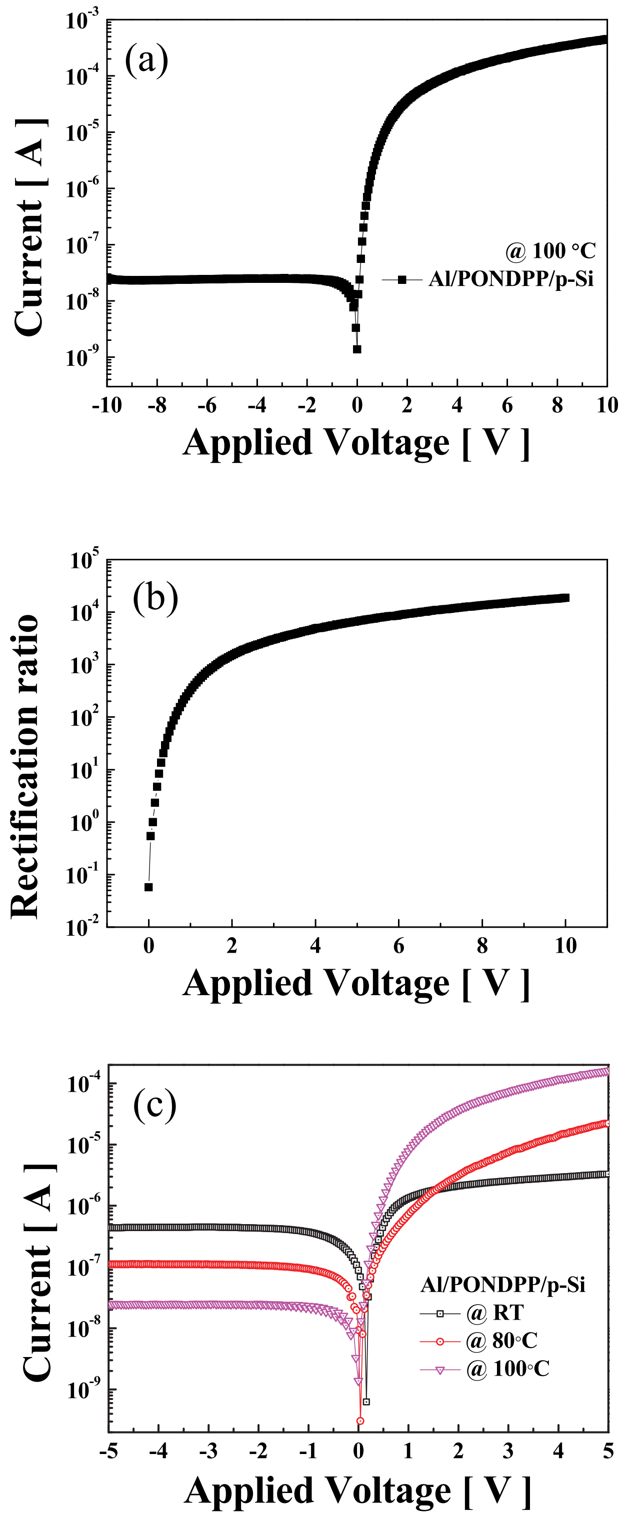

FIG. 3. (a) The current to voltage curves of Al/PONDPP/p-Si/Al Schottky diode at annealing temperature of 100 °C. (b) The rectification ratio curve versus applied voltage of Al/PONDPP/p-Si/Al at 100 °C. (c) The current to voltage curves of Al/PONDPP/p-Si/Al Schottky diode at annealing temperature of room temperature, 80, 100 °C, respectively.

We found that the calculated parameters of ideality factor and barrier height for Al/PONDPP/p-Si/Al are 2.67 and 0.68 eV, respectively. The higher value of ideality factor means non-ideal diode behavior that originates from the voltage drop by series resistance and the interface states.[22] Also, the combination of recombination and diffusion currents at hole accumulation/depletion junction with p-Si incur deviation of ideality factor from unity. Figure 3(c) shows the dark current curves of Al/PONDPP/p-Si/Al diode when the annealing temperature of device is varied from room temperature to 100 °C. The reverse bias current to voltage characteristics gives information about the properties of metal to semiconductor contact. The reasons for the higher reverse current before post annealing are the recombination of charge carriers at Al/PONDPP, release of charge carriers from trap levels, and barrier lowering at high electric field.[23,24] This mechanism is clarified from the calculated increased barrier height as annealing temperature increases. The values of barrier height are 0.60, 0.64, and 0.68, respectively. In forward bias region, the lowering current at higher voltage regions are attributed to the SCLC (space charge limited conductivity) and the serial resistance by trapping level from solvents. And, the thermal budget from higher annealing temperature encourages the molecular pi-bonding and hole transport.[25,26] We note that the electrical performance of PONDPP Schottky diode could be further improved at higher annealing temperature in nitrogen atmosphere. Figure 4(a) shows the absorption spectra of PONDPP film. And, Fig. 4(b) is the reverse current versus voltage characteristics under the filtered light source for different wave length. As shown in Figure 4(c), the high responsivity of 55 mA/W is achieved at 650 nm. It is almost consistent with that of pristine PONDPP in the regions of 300 nm to 450 nm and 650 nm. The plot of responsivity versus wavelength is calculated using the following equation:

$$R = \frac{I_{ph}}{P_{opt}} = \frac{(I_{illum} - I_{dark})S^{-1}}{P_{inc}}, \quad (5)$$

I_{ph} is the photocurrent, P_{opt} is the incident light power, P_{inc} is the power of the incident light per unit area, I_{illum} is the current under illumination, I_{dark} is the current in the dark, S is the effective device area, and R is the responsivity. Figure 5(a) shows the photo-response characteristics of PONDPP Schottky diode as light power increased. The current on-off ratio value for the diode under 100 mW/cm^2 is 2.69×10^2. In Figure 5(b), it is seen that I_{ph} ($I_{illum}-I_{dark}$) is almost linear to the increased light intensity. The photo-response characteristic of PONDPP Schottky diode shows very uniform reverse saturation current than other reported organic-silicon Schottky diode with conventional p-type organic semiconductor via solution process.[27,28] This property reveals that the PONDPP has enhanced thin film stability and low dark current generation due to carrier recombination. Therefore, we can conclude that the photoconductive characteristics of Al/PONDPP/p-Si/Al can be applied to the photo-detector, which is fine compared to other materials in spite of the degradation under repeated light illumination.[29–31] We note that the fine photoconductivity characteristics of our devices are mainly attributed to efficient hole transporting by high hole mobility of PONDPP despite the non-zero HOMO-E_v offset that impedes effective exciton dissociation.

In conclusion, we introduced Al/PONDPP/p-Si/Al for Schottky diode using the donor-acceptor alternating copolymer of PONDPP as p-type organic semiconductor via solution process. The demonstrated device reveals fine electrical and photoconductive properties as the Schottky barrier exist

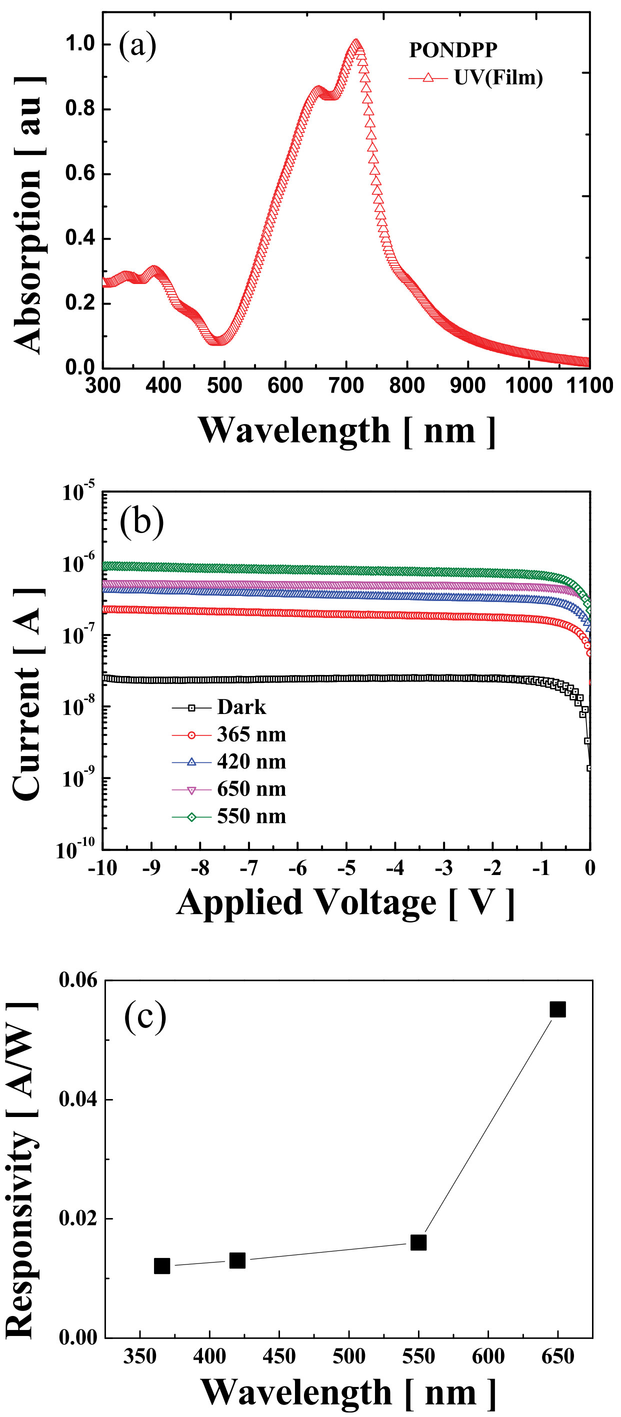

FIG. 4. (a) The absorption spectra of PONDPP film. (b) The reverse current to voltage curves of Al/PONDPP/p-Si/Al under varied wavelength. (c) The plot of photo-responsivity versus varied wavelength. The light intensity for 365 nm, 420 nm, 550 nm, and 650 nm is 5 mW/cm^2, 8.9 mW/cm^2, 15 mW/cm^2, and 3 mW/cm^2, respectively.

between the PONDPP and p-type silicon. The band structure between p-type organic and p-type inorganic junction contributes to the rectifying behavior and uniform reverse current. The experimented annealing temperature of devices show the feasibility of low temperature process under 100 °C. And the device shows high and stable photo-responsivity in the range of saturation region under varied light intensity and wave length. Therefore, we suggest that the PONDPP Schottky diode would be a promising candidate for the solution processed organic photoconductive devices.

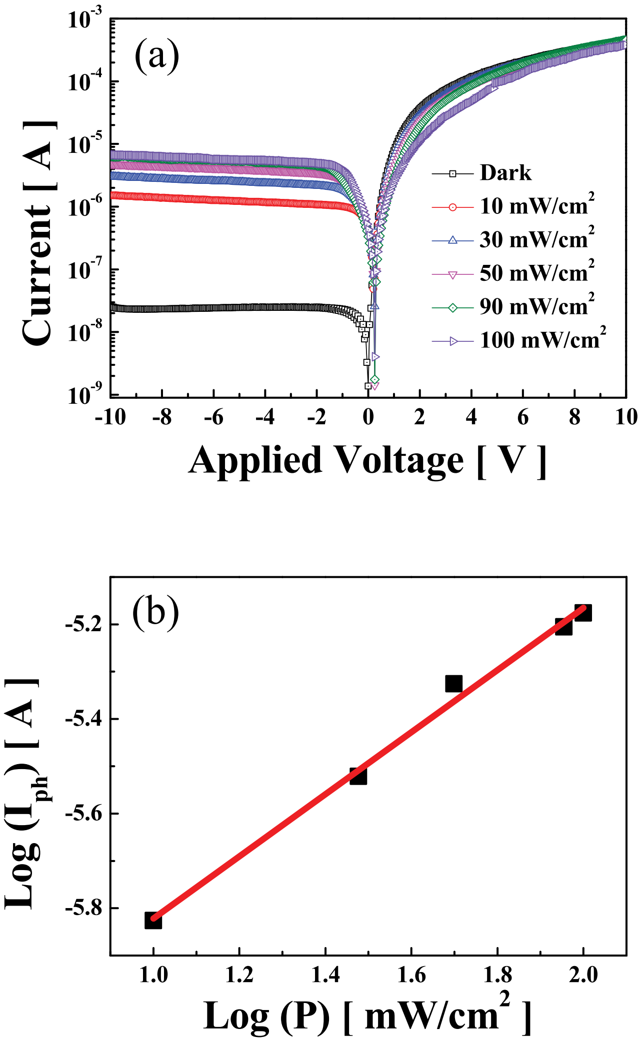

FIG. 5. (a) The current to voltage curves under light illumination, which is varied from dark to 100 mW/cm^2. (b) The plot of log (I_{ph}) versus log (P) of the Al/PONDPP/p-Si/Al Schottky diode.

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