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Improved electrical response of MIS diode with disperse orange-25 as insulator deposited by centrifugal process

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ABSTRACT

Disperse Orange-25 (OD-25), 3-[Ethyl[4-[(4-nitrophenyl)azo]phenyl]amino]-propanenitrile),has recently emerged as novel organic semiconductor form any electronics and optoelectronic devices. Here we investigate the electrical response of Silver/Orange-25 /Silicon (Ag/OD-25/Si) as Metal-Insulator-Semiconductor (MIS) diode, where OD-25thin-film was deposited by centrifugal process. We report different diode parameters such as series resistance, ideality factor, and density of interfacial state and interfacial barrier height as a function of processing parameter gravity acceleration. We find that high gravity acceleration improves the overall diode parameters, while the diode fabricated at 277g offers the most improved electrical response. Such improvement in diode parameters at gravity acceleration 277g is due to the formation of high quality OD-25interfacial layer for MIS diode.

Keywords: Organic Semiconductor, Orange Dye, Centrifugal thin film deposition, gravity acceleration, thermionic emission model, MIS diode.

INTRODUCTION

Thin-film deposition process plays a vital role to define the electrical response for organic electronic devices [1-3]. In order to optimize the electrical response, different thin-film deposition methods have already been reported for organic/polymer materials for their various electronic applications [4-7]. Among these methods, centrifugal thin-film deposition is a unique, simple, rugged and low cost method, especially for organic/polymer electronic devices [8-12]. Although centrifugal deposition process is being reported from last few years, but still it is not accepted for commercialization, one of the major reason for their non-commercialization is the complexities arises by the behavior of centrifugal processing parameters such as gravity acceleration during thin-film deposition process [13, 14].The centrifugal acceleration attains by samples during deposition process is generally expresses in terms of gravity acceleration (1g = 9.81m^2/s) and greatly affect the quality of thin film and hence electrical response of electronic device.

Similarly, the quality of organic thin film as insulator is a crucial factor for metal-semiconductor interface, which is highly suitable structure for efficient solar cell, metal-oxide field effect transistor (MOSFET), sensors and other types of electronic devices [15]. The interface properties between metal and semiconductor control the overall device performance both in term of efficiency and as well as stability [16, 17]. For efficient electronic devices, the formation of high quality metal-semiconductor barrier with low ideality factor, series resistance, and interfacial density of state is greatly desirable [17]. On the other hand, metal-insulator semiconductor diode is more attractive than the simple metal-semiconductor Schottky diode because the MIS diode shows much improved ideality factor, series resistance, and interfacial density of state parameters as compared to simple Schottky diode [18,19].

Recently, OD-25 shows some promising applications for solar cell, light emitting diode, electro-photography, gas-sensor, photo-sensor, thermal sensor etc. [3, 20-22]. Therefore, in this article we report and discuss the effect of high gravity acceleration during centrifugal deposition process on the quality of OD insulator for MIS diode in terms of different Schottky parameters.

MATERIALS AND METHODS

Disperse OD-25andother chemicals were purchased from sigma Aldrich and were used without any further purification, where the molecular structure of OD-25 is shown in Fig. 1. For thin film deposition, the 10% of OD-25 by weight was dispersed in water and stirred in an ultrasound container (Power Sonic 410)for more than 30 minutes. Meanwhile, thin film of aluminum metal as electrode was deposited on the back-side of pre-cleaned *n*-Si substrate (1-5 ohm.cm)for all diodes. For centrifugal thin-film deposition, aluminum deposited Si substrates were placed with OD-25solution in the vessels of desk-top centrifugal apparatus and operated at 1000 rpm (123g), 1500 rpm (277g) and 3000 rpm (1107g) in ambient environmental conditions. The detailed information about desk-top centrifugal apparatus can be found in our previously reported results [9, 10]. Just for comparison, OD-25 thin film was deposited over Si substrate in the same vessel of centrifugal apparatus under the same conditions but without any centrifugal rotation (1g)and waited nearly6 hours for OD-25 solidification. For electrical characterization, Ag as metal electrode was deposited on OD-25film in circular shape with ~5 mm diameter for all diodes. All the diodes were then annealed at 100°C for~ 1 hour in the inert environment of nitrogen gas. The schematic cross-section diagram of the finished device is shown in Fig. 2. The current-voltage characterization were measured by 4145B parameter analyzer.

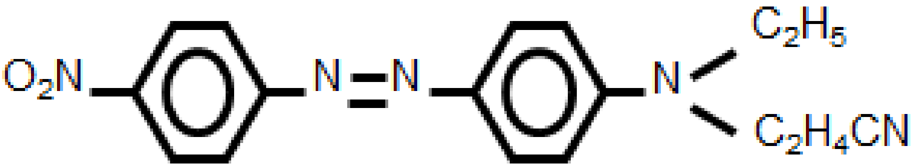

Figure 1. Molecular structure of OD-25

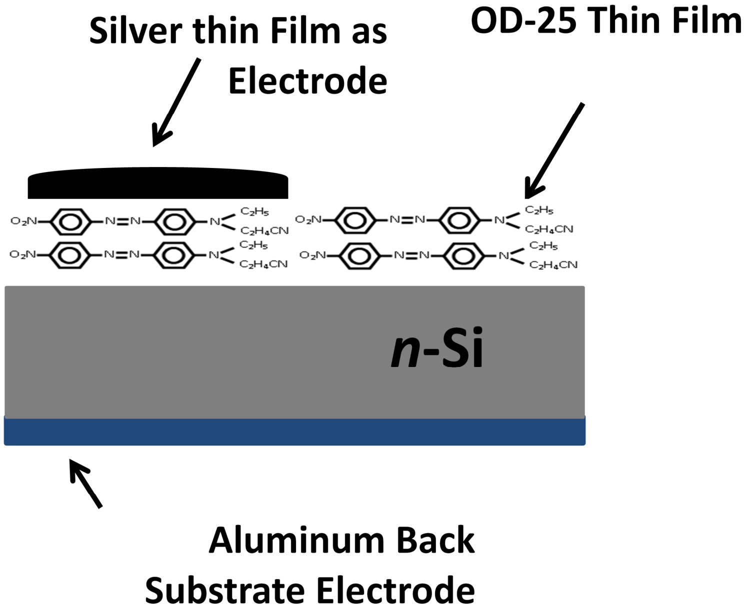

Figure 2. Schematic cross-sectional diagram of Ag/OD-25/Si diode, where organic OD-25layer is deposited over Si substrate (with aluminum as back sided electrode) by centrifugal deposition method at different gravity accelerations

RESULTS AND DISCUSSION

The current–voltage (*I*-*V*) characteristics of MIS diode fabricated at(a) 1g, (b) 123g, (c) 277g and (d) 1107g are shown in Fig. 3. From the figure it is clear that all diodes are demonstrating non-linear, typical asymmetric(rectifying) behavior as MIS diode with different current scales depending on the gravity acceleration. The MIS diode fabricated with higher gravity acceleration shows higher conductivity, while the diode fabricated at 277g shows the maximum conductivity. AsOD-25 has very low conductivity as compared to Si, therefore the I-*V* response for all MIS diodes is controlled by the interface between OD-25 and Si. Generally for MIS diode and especially for Si semiconductor, the thermionic emission model is used to define their I-*V* response [23-27]. The current (*I*) passing through the MIS diode can be modeled by thermionic emission equation with series resistance (R_s) as [23, 28-30]

$$I = I_o\left[\exp\left(-\frac{q(V-IR_s)}{nkT}\right)\right], \qquad (1)$$

where, I_o is the saturation current, q is the electric charge (1.602 x 10^{-19}C), IR_s is the voltage drop across the series resistance of a MIS diode, V is the applied voltage, n is the diode ideality factor, k (8.61733 x 10^{-5} ev/K) is the Boltzmann constant and T is ambient temperature (K). The I_o can be further define as [23]

$$I_o = AA^{*}T^{2}\exp\left(-\frac{q\Phi_b}{kT}\right), \qquad (2)$$

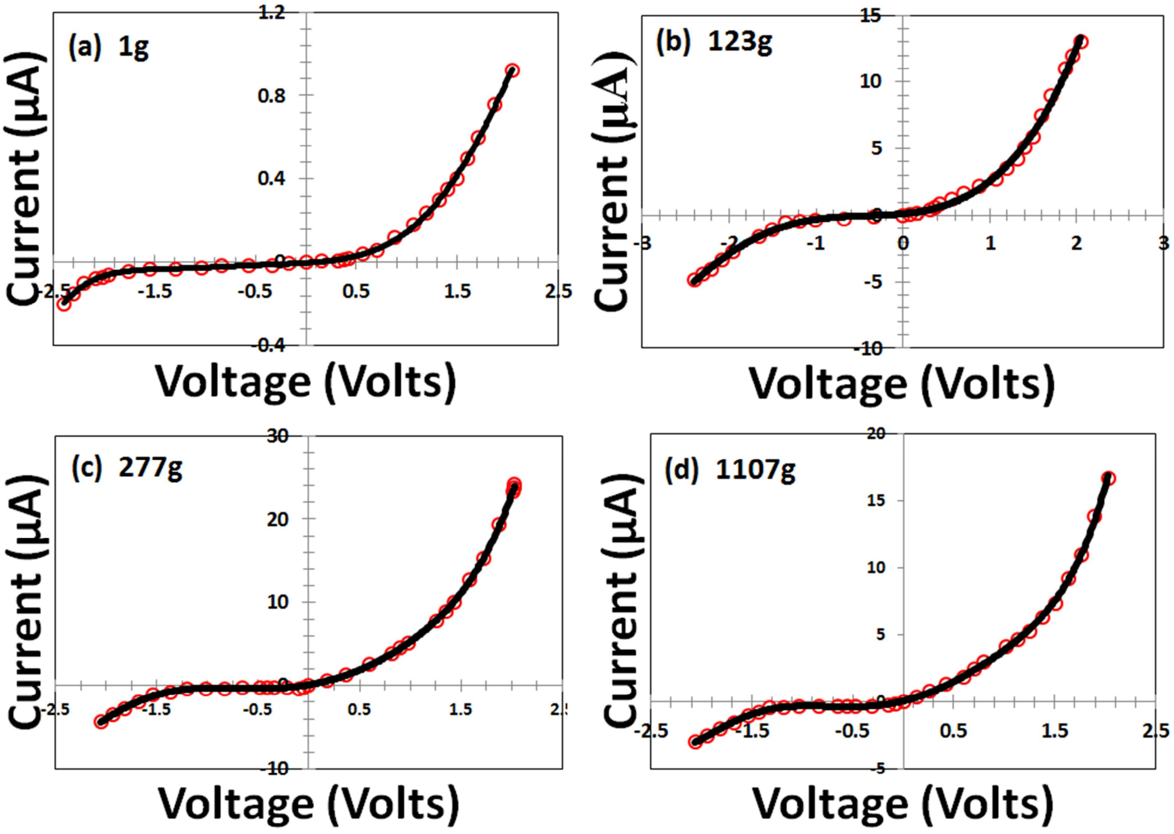

Figure 3. Current-voltage characteristics of Ag/OD-25/Si diode, where OD-25 was deposited over Si substrate at gravity acceleration of (a) 1g, (b) 123g, (c) 277g and (d) 1107g respectively

Where A is the effective area of diode, A^* is the effective Richardson-Dushman constant (10^{-2} A. cm^{-2} K^{-1}) and Φ_b is the effective barrier height (eV) between OD-25 and Si interface at zero biasing. By taking the natural logarithm, the equation 1 can be written as

$$\ell n\,(I) = \ell n\,(I_o) + \frac{q(V - IR_s)}{nkT}\ . \qquad (3)$$

Equation 3 can be further simplified by differentiating d [*ln(I)*]with respect to voltage and then after some manipulation can be written as

$$\frac{d\,[V]}{d\,[\ell n(I)]} = IR_s + \frac{nkT}{q} \qquad (4)$$

Plots between dV/d [*ln*(*I*)] and applied voltage for each diode are shown in Fig. 4.

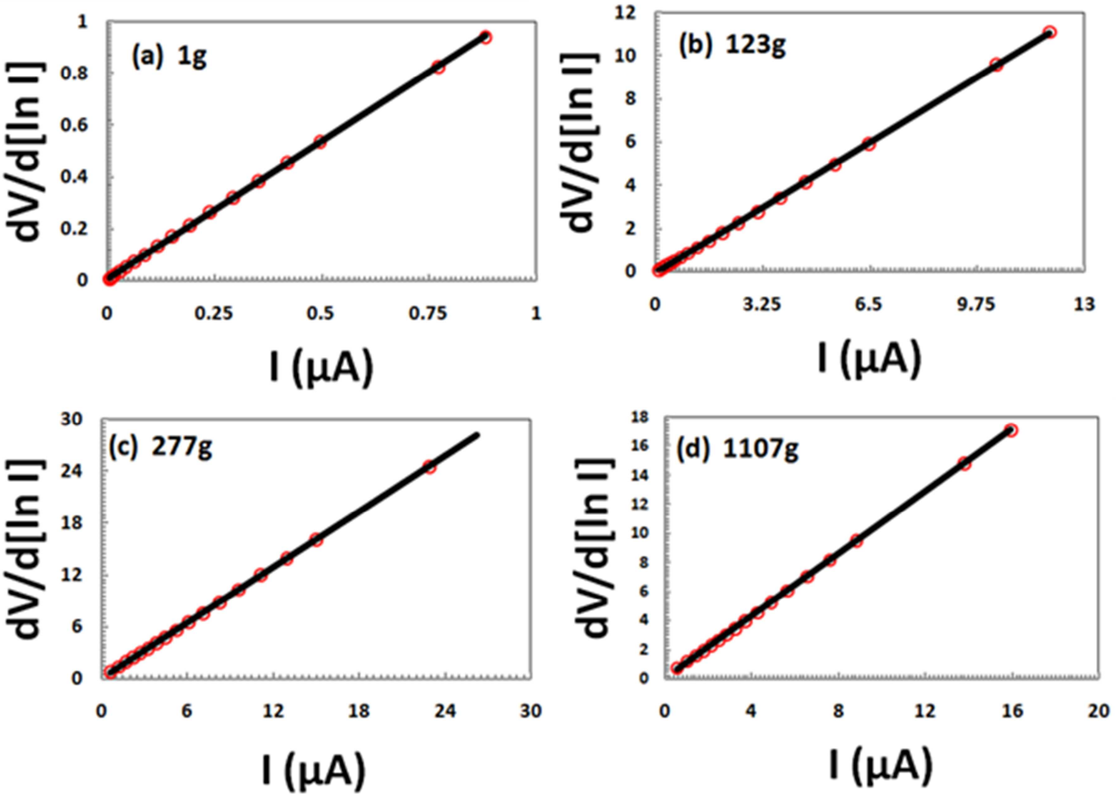

Figure 4. The dV/d [ln(I)] vs. I for Ag/OD-25/Si diode fabricated at gravity acceleration of (a) 1g, (b) 123g, (c) 277g and (d) 1107g respectively.

Figure clearly demonstrates that the junction between OD-25 and Si interface follow thermionic Richardson model for all devices fabricated at (a) 1g, (b) 123g, (c) 277g and, (d) 1107g respectively. The slope and y-intercept of a straight line shown in Fig. 4 gives us valuable information about barrier height and series resistance for MIS diode fabricated at (a) 1g, (b) 123g, (c) 277g , and (d) 1107g respectively.

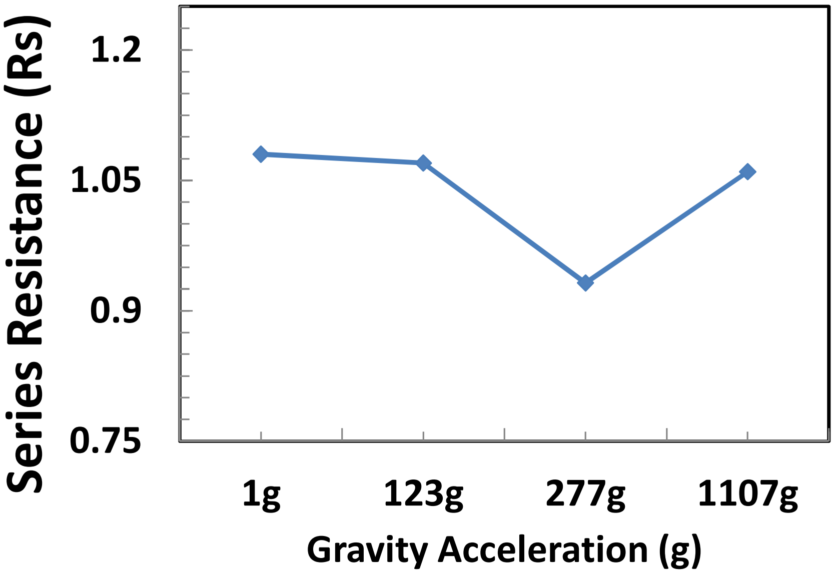

Figure 5. Series resistance (R_s) of Ag/OD-25/Si diode as a function of acceleration gravity used for the deposition of OD-25 over Si substrate

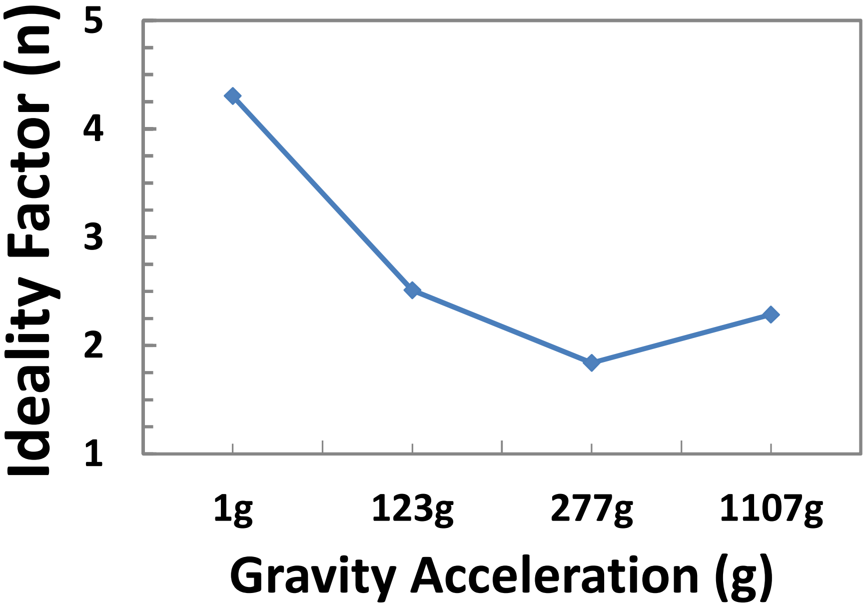

Figure 6. Ideality factor (*n*) of Ag/OD-25/Si diode as a function of acceleration gravity used for the deposition of OD-25 over Si substrate.

The series resistances were calculated for each diode are shown in Fig. 5 as a function of gravity acceleration 1g, 123g, 277g and 1107g respectively. Overall the series resistance is decreases when the gravity acceleration is increases. While the diode with OD-25 interface layer, deposited at277g, shows the minimum series resistance compare to the other diodes. The series resistance of MIS diode is the resultant resistance of both bulk Si and organic-Si interface resistance. Here bulk thickness of Si and organic layer is tried to keep constant for all diodes, therefore we assume that reduction of observed resistance is mainly due to the reduction in the interface resistance.

Similarly, Fig. 6 shows the behavior of ideality factor as a function of gravity acceleration during thin film deposition process. Ideality factor is extracted by curve fitting method as discuss above and it correlates the electrical behavior of actual diode with the electrical response of a theoretical diode (n =1). Figure clearly indicates that all diodes show higher value (> 1) of ideality factor and overall ideality factor is improved when OD-25 is deposited at high gravity acceleration, while diode with OD-25 thin film deposited at 277g shows best ideality factor.

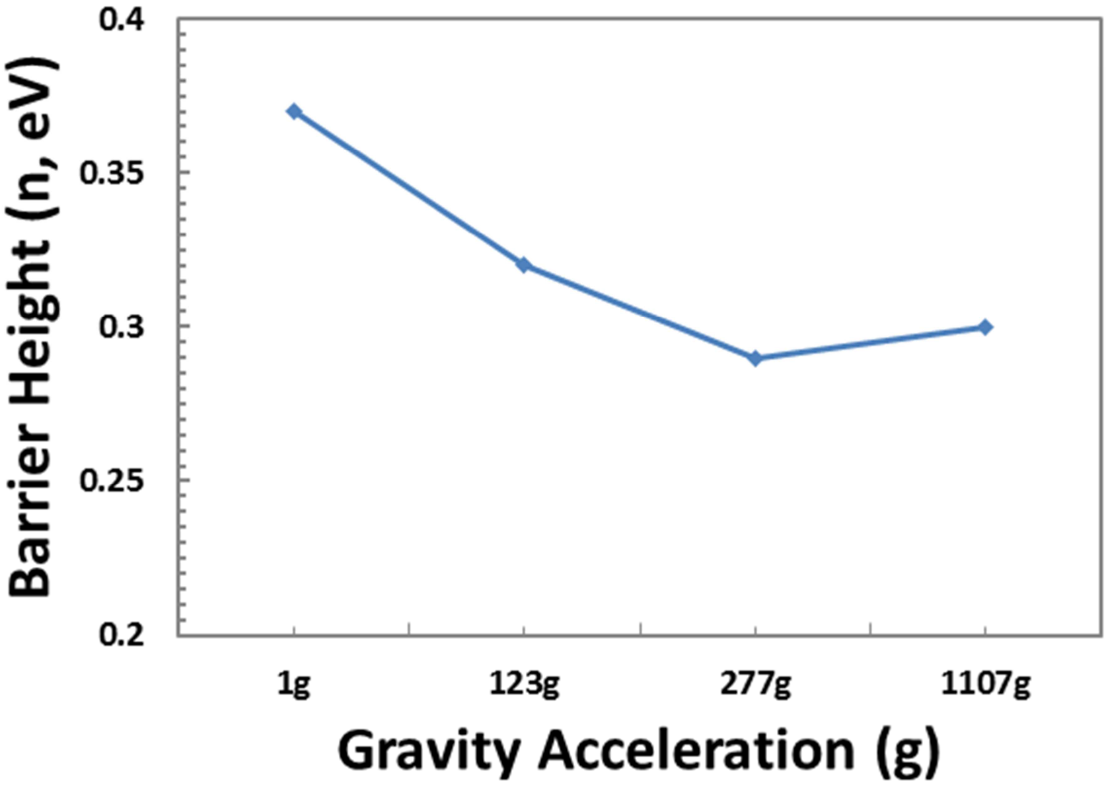

Figure 7. Barrier height (Φ_b) between metal-Si interface in the presence of OD-25 interfacial layer, where OD-25 thin film was deposited at gravity acceleration of (a) 1g, (b) 123g, (c) 277g and (d) 1107g respectively

Another important parameter, barrier height between OD-25 and Si interface can be calculated by manipulating equation 2 as [30]

$$H(I) = V - n\left(\frac{kT}{q}\right)\ell n\left(\frac{I}{AA^{*}T^{2}}\right) \qquad (5)$$

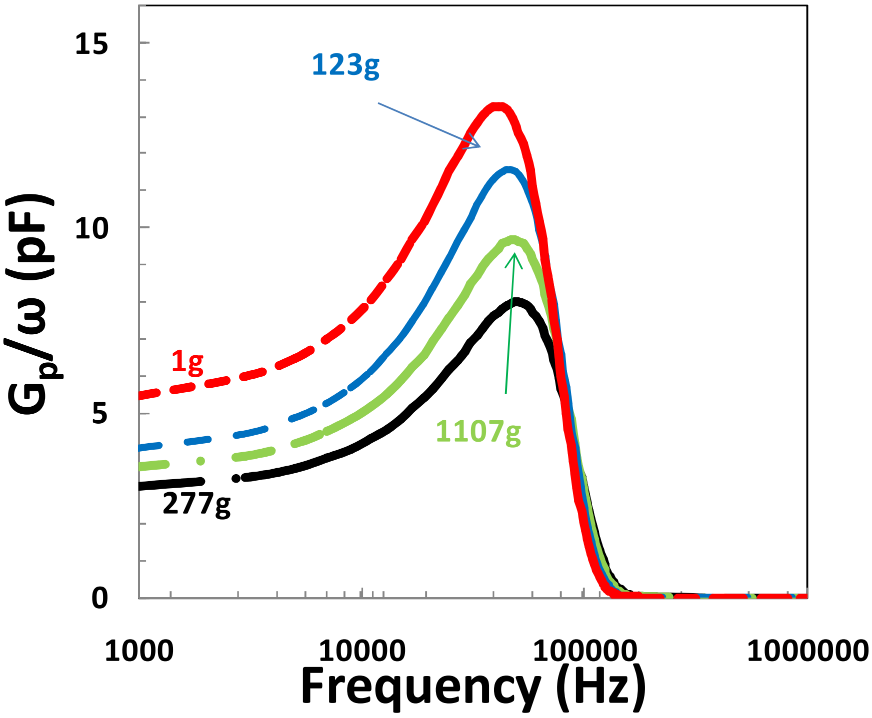

Figure 8. Plots of (Gp/ω) vs. frequency for metal-Si interface in the presence of OD-25 interfacial layer, where OD-25 thin film was deposited at gravity acceleration of (a) 1g, (b) 123g, (c) 277g and (d) 1107g respectively.

$$H(I) = IR_s - n\Phi_b \qquad (6)$$

Firstly H(I) is calculated from equation 5 for each diode fabricated at (a) 1g, (b) 123g, (c) 277g and (d) 1107g respectively, which helps to calculate barrier height for MIS diodes fabricated at 1g, 123g, 277g and 1107g respectively. Figure 7 shows the relation between barrier height and gravity acceleration for MIS diode, again more or less similar series resistance trend is observed. Barrier height directly depends on gravity acceleration attains by the substrate during centrifugal thin film deposition method. Barrier height is decreases when the gravity acceleration is increases and the minimum barrier height is observed for MIS diode fabricated at 277g gravity acceleration.

Another important parameter, density of Interfacial state (D_{it}), is also investigated to further compare the quality of interfacial organic layer for MIS diode. To obtain D_{it}, the parallel conductance (G_p) for each diode were measured over a wide range of frequency from 1 kHz to 1 MHz at 1.0 applied voltage under ambient temperature conditions [32]. The maximum value of conductance/angular frequency ($(G_p/\omega)_{max}$, $\omega = 2\pi f$) can be correlate to the D_{it} for MIS diode as [32, 33]

$$D_{it} = \frac{1}{0.4qA}\left(\frac{G_p}{\omega}\right)_{\max} \tag{7}$$

Here, *A* is the area of metal electrode. The measured G_p/ω as a function of ω for MIS diode with OD-25 layer deposited at (a) 1g, (b) 123g, (c) 277g, (d) 1107g are plotted in Fig. 8 and the density of interfacial state (D_{it}) were calculated for each diode and are shown in Fig. 9.Figure demonstrate that the $(Gp/\omega)_{max}$ is decreases when the gravity acceleration is increases and the diode fabricated at 277g shows the minimum $(Gp/\omega)_{max}$ and hence density of interface state. Therefore, the observed reduced density of state for277g diode may be due to the improved quality of OD-25 layer between metal and Si substrate as compared to the other diodes.

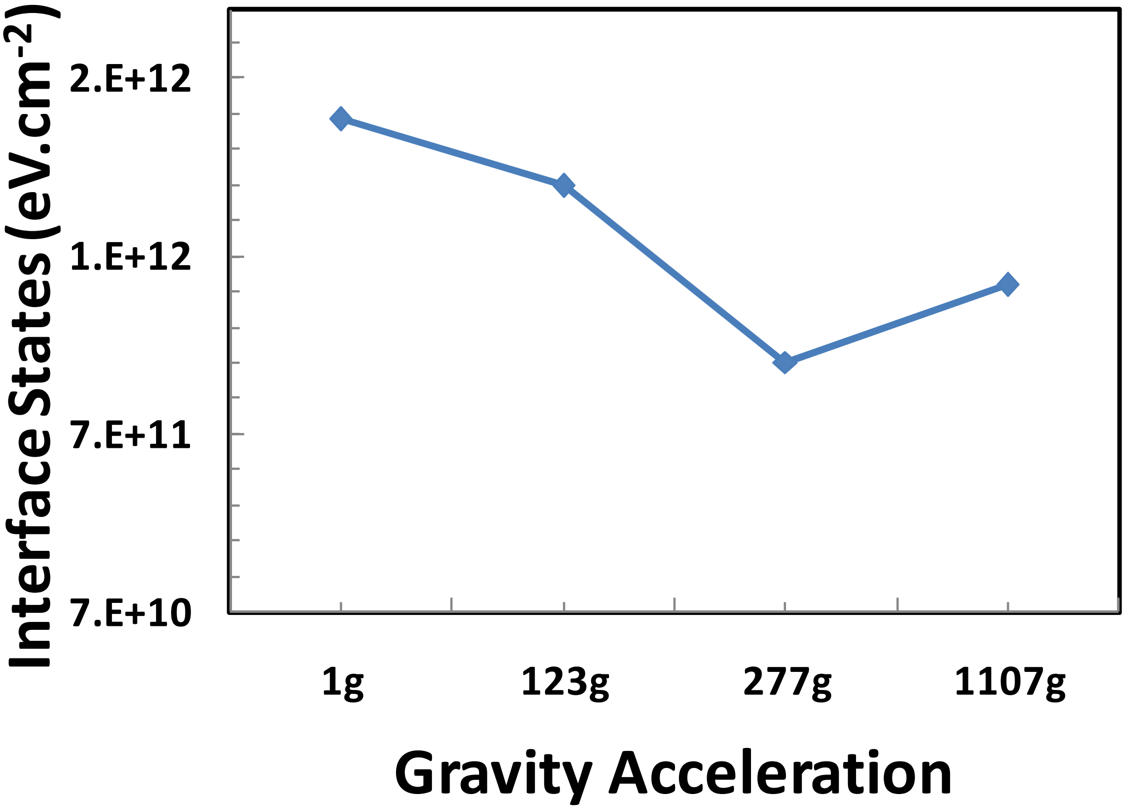

Figure 9. Density of state between metal-Si interface in the presence of OD-25 interfacial layer, where OD-25 thin film was deposited at gravity acceleration of (a) 1g, (b) 123g, (c) 277g and (d) 1107g respectively

The trends of ideality factor, series resistance, interfacial barrier height and interface state density clearly demonstrate that the overall interfacial behavior of OD-25 and Si junction is improved by high gravity acceleration processing parameter. Generally the interface between organic and Si can be considered as the full occupation of dangling and strained bonds due to surface abruptness, micro-roughness and lattice mismatch [34, 35].It is unanimously accepted that high quality organic thin film passivates these dangling and strained bonds, which in turn improves the organic-Si interface and can be inferred from their Schottky parameters [36-38]. Therefore, we can justify that the observed improvement in series resistance, ideality factor, interfacial barrier height and interfacial state density at high gravity acceleration is mainly due to the improvement in quality of OD-25 thin film deposition at high gravity acceleration.

Now question arises, why MIS diode fabricated at 277gshows the best Schottky response. In this regards, Regel and others[39-43]explored the centrifugal process in detail for the growth of both crystalline and non-crystalline semiconducting materials and they observed similar trend of high quality semiconductor rfilm at particular gravity acceleration during crystal growth process. They investigated both experimentally and theoretically the centrifugation process with many models such as flow transition model, thermal stability model and buoyancy-coriolis balance model and proposed that the good quality thin film is formed due to the maximum suppression of convection process, at some suitable gravity acceleration during centrifugal process [31,42].

Similarly, centrifugal thin film deposition method for organic/polymer thin film is also very complex. Many factors such as buoyancy, hydrostatic, thermal, vibration and coriolis forces play an active role during centrifugal thin film deposition process. Many of these forces are interdependent and make It challenging to control them during film deposition process. When organic solution is placed in vessel, the organic molecules are dispersed in the solvent on the surface of Si substrate. During centrifugation process all of these forces, especially buoyancy force act on organic molecules and cause them to push towards their outer peripherals of substrate, and trigger the evaporation process. Many thin film processing factors such as thinning, evaporation of solution, and orientation of organic molecules may improves at higher gravity acceleration and are optimized at 277g to give rise good qualityOD-25 thin film MIS diode, as revealed by Schottky parameters.

CONCLUSION

In summary, the electronic properties of Ag -Si diode were investigated and discussed in the presence of OD-25 interfacial layer, where OD-25 interfacial layer were deposited at various gravity acceleration during thin film deposition process. The quality of diodes parameters such as series resistance, ideality factor, interface barrier height and density of interface state were evaluated and compared as a function of gravity acceleration during thin film deposition process. It was observed that diode parameters were improved at higher gravity acceleration and the most improved diode parameters were observed for Ag/OD-25/Si diode fabricated at 277g during centrifugal deposition process. Such improvement in barrier height, series resistance, interfacial state density and ideality factor at 277g can be attributed to the good quality of OD-25 thin film for MIS diode. Therefore, it can be concluded that the quality of organic semiconductor thin film as interfacial layer can be optimized for efficient MIS diode by using proper gravitational acceleration during centrifugal thin film deposition process.

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