

Preparation and characterization of CdSe, ZnSe and CuSe thin films deposited by the successive ionic layer adsorption and reaction method

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In this study, the CdSe, ZnSe and CuSe thin films have been directly formed on n-type Si by means of Successive Ionic Layer Adsorption and Reaction (SILAR) method, at room temperature. The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). The SEM and XRD studies showed that films covered well n-type Si substrates and exhibit polycrystalline phase. The EDAX spectra showed that the expected elements exist in the thin films. Some of the thin film with equal distribution of grains, mostly falling in nanometer regime, was clearly seen. Additionally, Cd/CdSe/n-Si/Au-Sb, Zn/ZnSe/n-Si/Au-Sb and Cu/CuSe/n-Si/Au-Sb structures are prepared by the SILAR method at room temperature. The characteristics parameters such as ideality factor (n), barrier height (Φ_b) and saturation current (I_0) are obtained from current-voltage (I-V) measurement by applying a thermionic emission theory. According to the optical and electrical characterizations, in the future, these can be used for solar-cell studies, rectifying contacts, integrated circuits, other electronic devices and so on.

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1. Introduction

Semiconductors are generally prepared by high temperature solidification methods from the elements in bulk form, or vapor phase and vacuum methods in the form of thin films. Liquid solutions, using water or other solvents (organic, ionic liquids, molten salts), represent other phases from which the growth of materials either in bulk form or as thin films is possible [1].

CdSe, ZnSe and CuSe materials can be deposited in bulk and thin-film form by different methods such as chemical vapour deposition, metal-organic chemical vapor deposition, molecular beam epitaxy, pulsed laser deposition, chemical spray and sol-gel technique [2-15]. In this paper, we report the preparation and characterization of CdSe, ZnSe and CuSe thin films deposited by a simple Successive ionic layer adsorption and reaction (SILAR) method [16-18].

SILAR method is one of the solution methods. This method is mainly based on immersion of the substrate into separate cation and anion precursor solutions and rinsing between every immersion with ion exchanged water to avoid homogeneous precipitation.

In spite of its simplicity, SILAR has a number of advantages: unlike physical technique, SILAR does not require high quality target and/or substrates nor it does require vacuum at any stage; the deposition rate and the thickness of the film can be easily controlled over a wide range by changing the deposition cycles; it offers extremely easy way to dope films; there are virtually no restrictions on substrate material, dimensions or its surface

profile; moreover, it is convenient for large area deposition [19, 20].

In this paper, we report the firstly successful directly deposition of nanocrystalline CdSe, ZnSe and CuSe thin films on single crystal n-type Si (111) wafer substrates using SILAR method. These films are characterized for their structural properties by using XRD, SEM and EDAX measurement techniques. The Cd/CdSe/n-Si/Au-Sb, Zn/ZnSe/n-Si/Au-Sb and Cu/CuSe/n-Si/Au-Sb sandwich structures are prepared using by SILAR method and the dark I-V characteristics of these structures were studied at room temperature.

2. Experimental

In this study, to fabricate the above proposed structures, cleaned and polished n-type Si semiconductor with (111) orientation and 1-10 Ω -cm resistivity was used. The wafer was dipped in i.e. 10 min boil $\text{NH}_3 + \text{H}_2\text{O}_2 + 6\text{H}_2\text{O}$ solution and followed by a 10 min $\text{HCl} + \text{H}_2\text{O}_2 + 6\text{H}_2\text{O}$ at 60 °C. The native oxide on the front surface of the substrate was removed with $\text{HF} + \text{H}_2\text{O}_2$ (1:10) solution and then followed by rinse in de-ionized water of 18 M Ω . Zinc selenide thin films were deposited using ZnCl_2 , Cadmium selenide thin films were deposited using CdCl_2 and CuSe thin films were deposited using CuCl_2 for cationic solutions. The anionic solution was freshly prepared sodium selenosulphate (Na_2SeSO_3). The Na_2SeSO_3 solution was prepared by mixing 10 g selenium powder (99 % purity) with 100 gr anhydrous sodium sulfite in 500 ml of distilled water with constant stirring for 8-10 h at 80 °C. It was sealed and kept overnight, since on cooling, a little selenium separated out from the

solution. It was then filtered to obtain a clear solution.

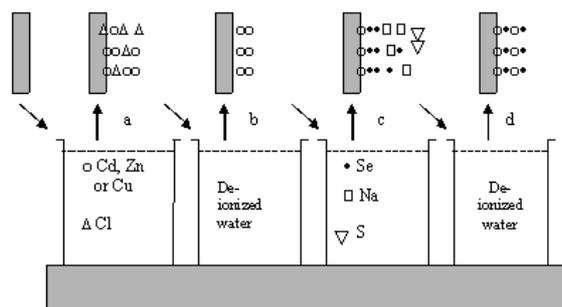


Fig. 1 Experimental scheme for the deposition of thin films.

The cationic and anionic precursor solutions characteristics; adsorption, reaction and rinsing times were detailed in literature for these thin films [16-18]. One SILAR cycle contained four steps: (a) the substrate was immersed into first reaction containing the aqueous cationic precursor, (b) rinsed with water, (c) immersed into the anion solution, and (d) rinsed with water. Fig. 1 shows the scheme of SILAR technique for the deposition of CdSe, ZnSe and CuSe thin films. Repeated these cycles, a solid solution CdSe, ZnSe and CuSe thin films with desired

thickness and composition were grown. By repeating such deposition cycles 50, 45, 55 times, we obtained these CdSe, ZnSe and CuSe thin films, respectively.

The ohmic contact was made by evaporating Au-Sb alloy on the back of the substrate, then, it was annealed at 420 °C for 3 min in N₂ atmosphere. After ohmic contact was made, the ohmic contact side and the edges of the *n*-Si semiconductor substrate was covered by wax so that the polished and cleaned front side of the semiconductor sample was exposed to the cationic precursor solution employed for SILAR method. To perform the electrical measurements, Cd, Zn, Cu were evaporated on the CdSe, ZnSe and CuSe thin films, respectively, at 10⁻⁵ Torr. In this way, Cd/CdSe/*n*-Si/Au-Sb, Zn/ZnSe/*n*-Si/Au-Sb and Cu/CuSe/*n*-Si/Au-Sb structures were obtained. A schematic cross-section of the sample holder together with the thin film/*n*-Si/Au-Sb device is shown in Fig. 2.

The films on *n*-Si substrate were characterized by their structural and optical properties by using X-ray diffractometer in the range of scanning angle 20-70° using Rigaku D/Max-IIIC diffractometer, ZEISS SUPRA 50VP scanning electron microscope with an attached energy dispersive x-ray analysis (EDAX) analyser to qualitatively measure the sample stoichiometry. The *I-V* characteristics of sandwich structures were measured using a HP 4140B picoammeter at room temperature and in the dark.

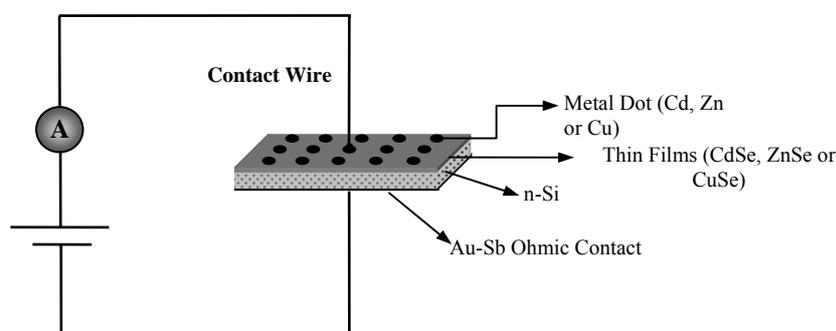


Fig. 2 Schematic cross-section of the sample holder and thin film/*n*-Si/Au-Sb device.

3. Results and discussion

The X-ray diffraction patterns are analysed to obtain the structural information of thin films. The structural analysis of CdSe, ZnSe and CuSe thin films were carried out by using X-ray diffractometer in the range of scanning angle 20-70°. The X-ray diffraction patterns of the as-grown on single crystal *n*-Si (111) substrates are shown in Fig. 3. The plane of Si (111) substrate is clearly observed in Fig. 3 and the plane intensity is dominant compared with the others. The CdSe thin film spectrum exhibit sharp peaks which correspond to the diffraction from (002), (110) and (112) planes of hexagonal CdSe phase.

Zinc selenide can be grown with either hexagonal wurtzite type structure [Joint Committee of Powder Diffraction Standards [JCPDS card no: 15-105] or the cubic zincblende type structure [JCPDS card no: 37-1463]. It is seen from the XRD patterns that the ZnSe film is in polycrystalline orientation along different planes and phases. The XRD patterns in Fig. 3 confirms that the formed compound is ZnSe thin film with cubic structure polycrystalline with orientation along different planes and phases. It is to be specifically stated that each of these small peaks corresponds to the standard JCPDS file 47-1745 for the tetragonal Cu₃Se₂ phase in Fig. 3.

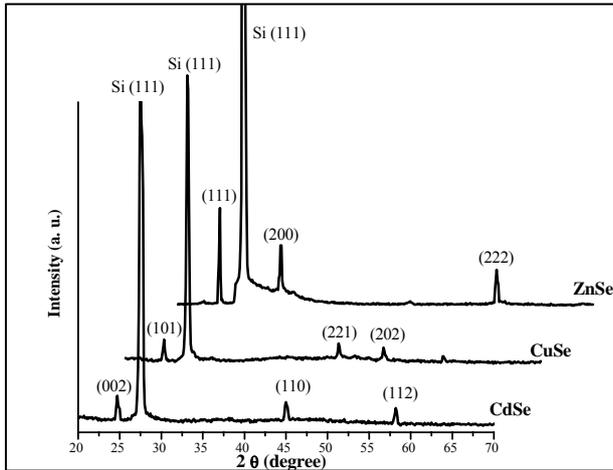


Fig. 3 XRD pattern of thin films grown on n-Si substrate.

Fig. 4, 5 and 6 show the SEM micrographs of these thin films. It can be observed that CdSe and ZnSe thin films are uniform, homogeneous and cover the substrates well without any voids, pinholes or cracks. From the CdSe micrograph it is clearly seen that the film, composed of small nanosized spherical grains. Also, Fig. 5 shows that the surface morphology of the ZnSe film on the Si was formed by grains, which have flower-like structure. The flower-like structures were observed on the entire film surface. From the CuSe micrograph it is clear that the grains are well defined, spherical, of almost similar sizes, which were almost uniformly distributed over a smooth homogeneous background.

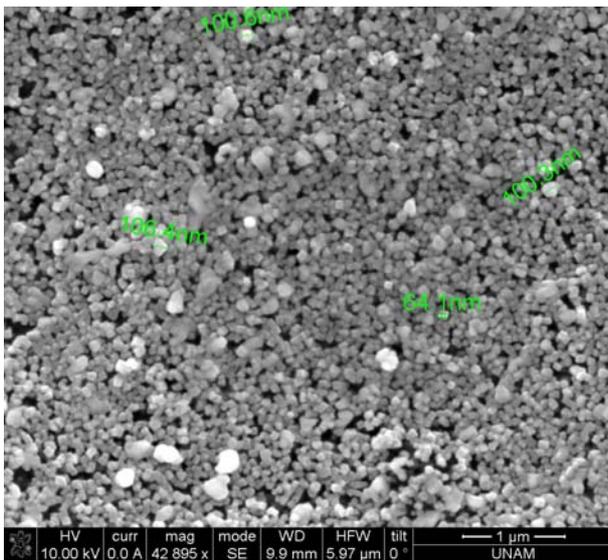


Fig. 4 SEM image of CdSe thin films grown on n-Si substrate.

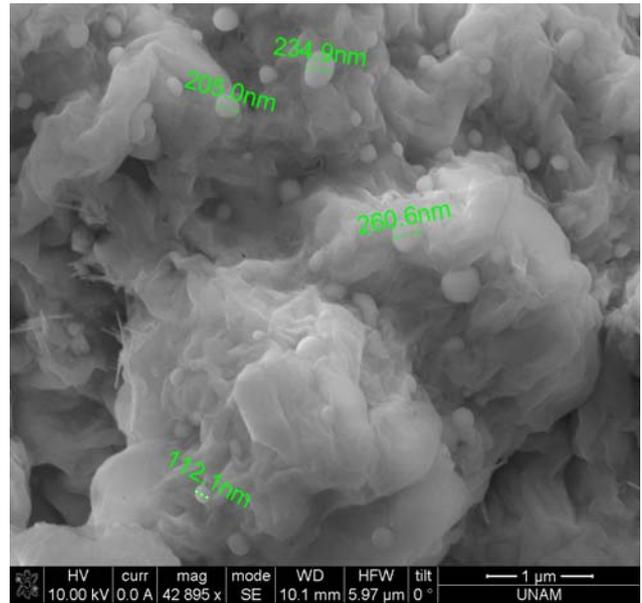


Fig. 5 SEM image of ZnSe thin films grown on n-Si substrate.

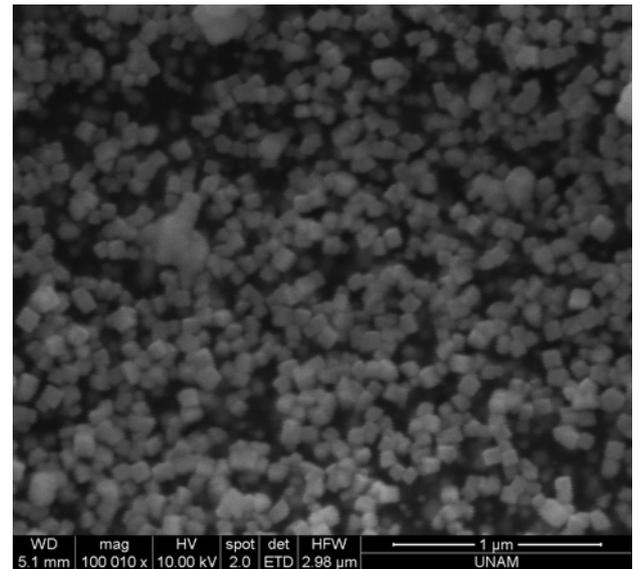


Fig. 6 SEM image of CuSe thin films grown substrate.

The quantitative analysis of the films were carried out by using the EDAX technique to study stoichiometry of films. Figure 7, 8 and 9 shows typical EDAX patterns and details of relative analysis for these thin films. These spectra show that the expected elements detected in the thin films. The elemental analysis was carried out only for (CdSe) Cd and Se; the average atomic percentage was found to be 20.82:9.81, for (ZnSe) Zn and Se; the average atomic percentage was found to be 27.01:13.23, for (CuSe) Cu and Se; the average atomic percentage was found to be 23.44:11.41. Also, small percentage of C and O elements are present in the thin films. It is thought that these elements may probably result from Si used as substrate.

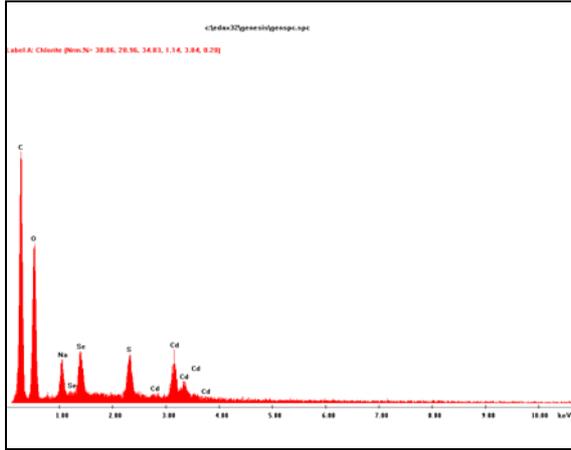


Fig. 7 EDAX spectrum of CdSe thin films grown on n-Si substrate.

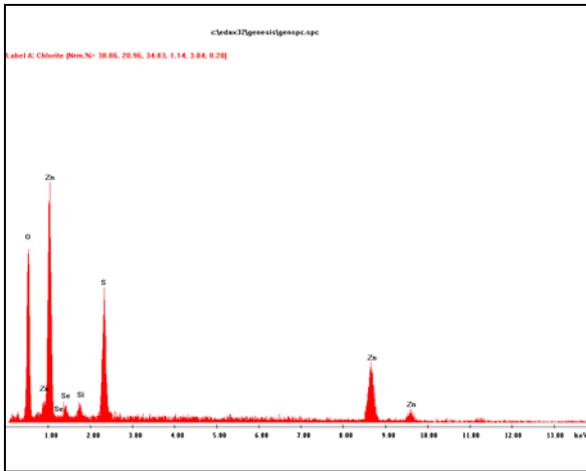


Fig. 8 EDAX spectrum of ZnSe thin films grown on n-Si substrate

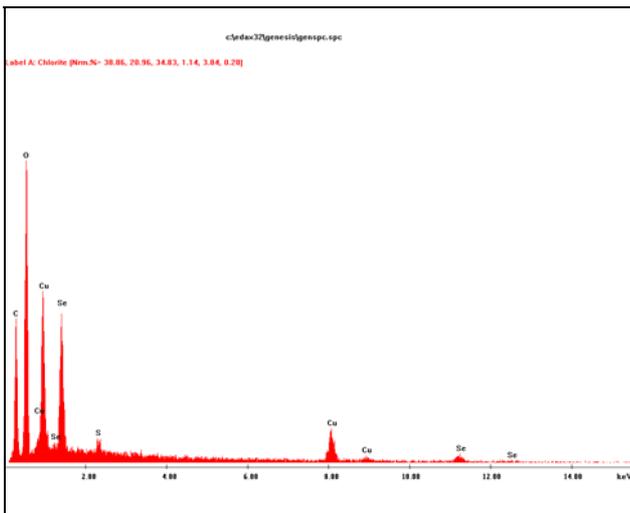


Fig. 9 EDAX spectrum of CuSe thin films grown on n-Si substrate

On the other hand, we prepared Cd/CdSe/n-Si/Au-Sb, Zn/ZnSe/n-Si/ Au-Sb and Cu/CuSe/n-Si/Au-Sb sandwich structures by means of SILAR method and investigated the electrical characteristics of these structures with $I-V$ measurement considering n , Φ_b and I_0 . The values of n were calculated from the slope of the linear regions of the forward bias $I-V$ characteristics in semilogarithmic scale. The barrier heights values were calculated from the y-axis intercepts of the semilog-forward bias $I-V$ characteristics.

When a MS structure with the is considered, the $I-V$ equation in respect to the thermoionic emission (TE) theory is given by [28]

$$I = I_0 \exp\left(\frac{eV}{nkT}\right) \left[1 - \exp\left(-\frac{e(V - IR_s)}{kT}\right) \right] \quad (1)$$

where n is the ideality factor, k is the Boltzmann constant, e is the electron charge, V is the forward bias voltage, T is the temperature, the series resistance and I_0 is the saturation current and is given by

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

A^* is the effective Richardson constant of 112 for n type Si, A is the area of the rectifier contact and Φ_b is the experimental zero bias barrier height, respectively. The value of ideality factor n can be obtained from Eq. (1) as,

$$n = \frac{e}{kT} \frac{dV}{d(\ln I)} \quad (3)$$

The barrier height values of Cd/CdSe/n-Si/Au-Sb, Zn/ZnSe/n-Si/ Au-Sb and Cu/CuSe/n-Si/Au-Sb sandwich structures were calculated by Eq. (2) from the y-axis intercepts of the semilog-forward bias $I-V$ plots, and the values of the ideality factor n was obtained using Eq. (3) from the linear region of these plots. The values of the parameters obtained from these characteristics are given in Table 1. Here, thin films on n-Si semiconductor are evaluated as the interfacial layer. For this reason, the Richardson constant of n-Si semiconductor used in calculating the barrier height ($A^* = 112$ for n type Si). The saturation current I_0 , deduced from the $I-V$ data by extrapolating the curves toward $V=0$, is used to obtain the zero bias barrier height. The barrier height, as well as the other diode parameters as the ideality factor n and the series resistance R_s can be calculated by means of a method developed by Norde [29,30,31,32]. The characteristics parameters obtained from the $I-V$ measurements are indicated in Table 1.

Table 1 The some parameters of Cd/CdSe/n-Si/Au-Sb, Zn/ZnSe/n-Si/ Au-Sb and Cu/CuSe/n-Si/Au-Sb sandwich sturctures obtained from the I-V measurements.

	I-V Measurement			
	n	Φ_b (eV)	I_0 (A)	R_s (k Ω)
Cd/CdSe/n-Si/Au-Sb	1.501	0.706	1.769E-8	1.262
Zn/ZnSe/n-Si/Au-Sb	1.217	0.779	1.915E-9	1.245
Cu/CuSe/n-Si/Au-Sb	1.512	0.791	1.308E-8	2.056

Fig. 10, shows the forward and reverse bias I-V characteristics of the Cd/CdSe/n-Si/Au-Sb, Zn/ZnSe/n-Si/Au-Sb and Cu/CuSe/n-Si/Au-Sb sandwich structures, respectively. The rectifying ratio values range from 1043.229, 1513.243, 1283.22 in 0.5 V, respectively. These structures were demonstrated clearly good rectifying behaviour at room temperature.

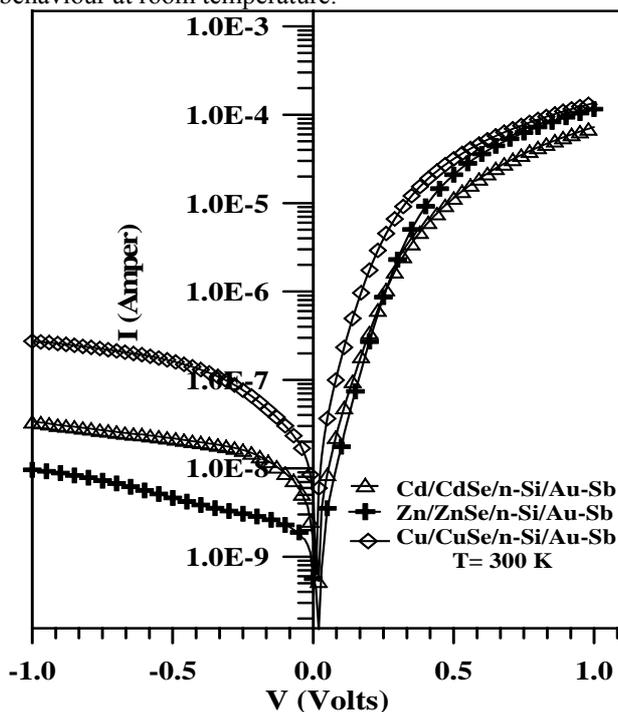


Fig. 10 The semi-log forward and reverse bias current-voltage characteristics of sandwich structures at room temperature.

The Cd/CdSe/n-Si/Au-Sb, Zn/ZnSe/n-Si/ Au-Sb and Cu/CuSe/n-Si/Au-Sb sandwich structures has demonstrated clearly rectifying behavior by the current-voltage curves studied at room temperature. Because of interfacial layers, these structures were evaluated as MIS diode. Therefore, the current-voltage characteristics are asymmetric. That is, in the forward bias, current flows

through the structure and in the reverse bias, current does not flow through the structure. Therefore, these structures are considered as diode. Barrier height is inversely proportional to saturation current according to Eq. (2). Saturation currents were calculated from the y-axis intercepts of the semilog-forward bias current-voltage plots. However, rectification ratio is the ratio between the forward and reverse currents in the same forward and reverse bias voltage values.

4. Conclusions

In this study, the SILAR method was used to deposit CdSe, ZnSe and CuSe thin films on Si substrates. The structural properties of these thin films were investigated by XRD, SEM and EDAX methods. The crystal structures of the CdSe, ZnSe and CuSe thin films were investigated by X-ray diffractometer and their main diffraction peaks are found to be in agreement with the other studies. The films were found to have polycrystalline, homogeneous and covered the substrates well. The EDAX spectra showed that the expected elements exist in these thin films. Some of the thin film with equal distribution of grains, mostly falling in nanometer regime, was clearly seen. Cd/CdSe/n-Si/Au-Sb, Zn/ZnSe/n-Si/Au-Sb and Cu/CuSe/n-Si/Au-Sb sandwich structures were demonstrated clearly good rectifying behavior at room temperature. According to the optical and electrical characterizations, in the future, these structures could be used in applications like: solar-cell studies, rectifying contacts, integrated circuits, and other electronic and optoelectronic devices.

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