Ultra wide bandgap amorphous oxide semiconductor, Ga-Zn-O

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ABSTACT

We fabricated amorphous oxide semiconductor films, $a\text{-(Ga}_{1-x}\text{Zn}_x\text{)O}_y$, at room temperature on glass, which have widely tunable band gaps (E_g) ranging from 3.47 – 4.12 eV. The highest electron Hall mobility $\sim 7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was obtained for $E_g = \sim 3.8 \text{ eV}$. Ultraviolet photoemission spectroscopy revealed that the increase in E_g with increasing the Ga content comes mostly from the deepening of the valence band maximum level while the conduction band minimum level remains almost unchanged. These characteristics are explained by their electronic structures. As these films can be fabricated at room temperature on plastic, this achievement extends the applications of flexible electronics to opto-electronic integrated circuits associated with deep ultraviolet region.

Keywords: Amorphous oxide semiconductor, band alignment, ionization potential, electron traps

1. Introduction

Amorphous oxide semiconductor (AOS) thin-film transistor was firstly reported in 2004 [1] and have attracted much attention due to their promising properties such as high transparency, high electron mobility, flexibility, and low-temperature process compatibility. In ionic oxide materials like AOS, conduction band (CB) minimum (CBM) is formed mainly by unoccupied metal ns -orbitals (n = principal quantum number), while fully-occupied O 2p orbitals contribute mainly to the valence band maximum (VBM) [2–4]. Therefore, large overlap between the ns -orbitals of next neighboring cations intervening an oxygen leads to large CB dispersion and high electron mobility even in an amorphous structure as demonstrated for amorphous In-Ga-Zn-O (a-IGZO) [1, 2]. However, these materials including a-IGZO suffer from instability against visible light illumination although their bandgaps (E_g) are typically larger than 3.0 eV. It is due to defect states just above VBM (near-VBM states), [5,6] which causes subgap optical responses from the photon energy ~ 2.4 eV [7]. To overcome this issue, we here propose ultra wide band gap AOS with significantly large band gaps $\gg 3.0$ eV, where even subgap states do not cause the visible light absorption. To date, a variety of crystalline transparent conductive oxides (TCOs) have been reported; however, most of them contain the representative TCOs of ZnO, In_2O_3 , SnO_2 , and Ga_2O_3 as major constituents. Development of AOSs has followed a similar manner, leading to a-In-Zn-O, a-Zn-Sn-O, a-In-Ga-O,

a-In-Sn-Zn-O, a-Sn-Ga-Zn-O, a-Hf-In-Zn-O, a-Ga-Cd-O [1,8–11], etc. Among the crystalline TCOs, pure β -Ga₂O₃ has the largest E_g of 4.9 eV [12]; however, electron conduction in pure amorphous Ga₂O₃ (a-Ga₂O₃) has not yet been reported.

In this work, we investigated amorphous thin films in the (Ga_{1-x}Zn_x)O_y system, and obtained semiconducting amorphous films from $x = 0$ to 0.65, where E_g ranged from 3.47 – 4.12 eV and the highest mobility of $\sim 7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was obtained for $E_g = 3.8 \text{ eV}$.

2. Experimental details

All thin films were fabricated by pulsed laser deposition using a KrF excimer laser (wavelength: 248 nm) in an O₂ gas flow at room temperature on silica glass substrates. We synthesized polycrystalline ceramic targets with four different chemical compositions, ZnO, (Ga_{0.35}Zn_{0.65})O_y, (Ga_{0.7}Zn_{0.3})O_y, and Ga₂O₃. The targets were prepared from powders of ZnO (purity, 99.999%) and Ga₂O₃ (purity, 99.99%), which were sintered at 1500 °C for 5 hours in air. Oxygen pressure (PO_2) during deposition and laser fluence were varied 1 – 4 Pa and 1 – 4.5 J/cm², respectively. Pulse repetition was fixed at 10 Hz. Some films were subjected to post-deposition thermal annealing at $T_a = 200 - 600 \text{ °C}$ in vacuum.

Film structures and thickness' were characterized and determined by high-resolution X-ray diffraction (HR-XRD) and grazing-incidence X-ray reflectivity (GIXRR), respectively. Optical

band gap values were estimated by Tauc' plots for amorphous films while that of crystalline ZnO was taken from a literature. Electrical properties were measured by Hall effect with the van der Pauw configuration. Desorption of constituents was measured by thermal desorption spectroscopy (TDS). Chemical composition was analyzed by X-ray fluorescence (XRF) spectroscopy, where the chemical compositions were calibrated using the results of inductively coupled plasma atomic emission spectroscopy.

The energy levels of CBM and VBM were measured by ultraviolet photoemission spectroscopy (UPS, excited by He I and II light sources). To prepare chemically pure surfaces, Ar ion sputtering was conducted for 1 hour at an acceleration voltage of 1 kV in a vacuum chamber connected to the UPS measurement chamber. Work function was determined from the cut-off energy of secondary electrons, and ionization potential (I_p) was estimated by combining the work function and the measured valence band maximum level [13]. Electron affinity (χ) was speculated using the band gap by $\chi = I_p + E_g$.

3. Results and Discussion

3.1 Deposition condition to obtain amorphous (Ga_{0.35}Zn_{0.65})O_y

We first investigated effects of laser fluence and T_a on (Ga_{0.35}Zn_{0.65})O_y thin films. As shown in Fig. 1(a), the thin film deposited at a low laser fluence (1.0 J/cm²) exhibited only

broad halos centered at $\sim 35^\circ$ and $\sim 63^\circ$ (the halo around 22° comes from the silica glass substrate), which indicates that the film is an amorphous phase. As the laser fluence increased, a sharp peak appeared at 32.62° , and the halos became sharper, suggesting formation and growth of crystallites. The full width at half maximum value of the halo at 32.2° for the highest laser fluence (4.5 J/cm^2) film was 1.93° , which corresponds to the crystallite size of 4.5 nm by the Scherrer equation. On the other hand, this peak position (32.2°) differs significantly from those of crystalline ZnO and $\beta\text{-Ga}_2\text{O}_3$; i.e., at 31.8° , 34.4° , and 33.5° for $10\text{-}10_{\text{ZnO}}$, 0002_{ZnO} , and $111_{\beta\text{-Ga}_2\text{O}_3}$ diffractions, respectively. Thus, it is possible that nanocrystals of solid-solution (Ga,Zn)O were deposited in these films at high laser fluences.

Then, we measured their chemical compositions and film densities using XRF and GIXRR. As summarized in Table 1, the film density was low, 5.27 g/cm^3 , for the low laser fluence of 1 J/cm^2 , but increased to 5.69 g/cm^3 with increasing laser fluence to 4.5 J/cm^2 . On the other hand, the chemical composition ratio Ga: Zn was almost unchanged at $\sim 65: 35$.

TDS spectra for H_2O (Fig. 1(c)) show that the low-density film deposited at the low laser fluence (1.0 J/cm^2) exhibited high-density desorption of H_2O molecules from $200\text{--}330^\circ\text{C}$. While, the high-density film deposited at 4.5 J/cm^2 exhibited much less H_2O desorption. It is known that high-density impurity hydrogen $> 10^{20} \text{ cm}^{-3}$ is contained in usual AOS such as a-IGZO deposited by conventional pulsed laser deposition and sputtering, which comes from

the residual gas in the deposition chamber and/or supplied gases [14]. These results suggest that the low densities of the lower laser fluence films are related partly to the incorporation of more H-related impurities such as H, H₂O, and OH. The incorporation of the impurities is enhanced at a lower deposition rate because the incorporation rate of hydrogen (i.e., number of hydrogen atoms per second) should be constant because it is determined by their densities in the residual/supplied gases, while a lower deposition rate requires a longer deposition time and consequently incorporate more impurities. Further, as it is reported that incorporation of H/H₂O stabilizes amorphous phases for (In,Sn)₂O₃ [15,16], In₂O₃ [17], etc, it is considered that the amorphous phase of the film deposited at 1 J/cm² would be stabilized also by the impurity hydrogen.

We next conducted post-deposition thermal annealing for the amorphous (Ga_{0.35}Zn_{0.65})O_y thin films deposited at 1.0 J/cm². As shown in Fig. 1(b), no distinct crystallization was observed up to 400 °C. While, a new halo feature appears at ~34.8° and its intensity started increasing from 500 °C. As the evolution of this halo is similar to that of the sharp peak detected in the 1.5 – 4.5 J/cm² films in Fig. 1(a), it is considered that the crystallization starts from a crystallization temperature (T_x) somewhere between 400 and 500 °C. As seen in Fig. 1(c), the H₂O desorption started from ~200 °C and depleted up to ~330 °C. This H₂O depletion temperature is obviously lower than the T_x , indicating that the crystallization in this (Ga_{1-x}Zn_x)O_y system requires extra

thermal energy other than the desorption of impurity hydrogen that would stabilize the amorphous phase in part.

In Fig. 1(d), we compared optical properties of thin films deposited with varied laser fluences. Polycrystalline- (poly-) $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ thin films deposited at 4.5 J/cm^2 exhibited higher Urbach tail-like absorption, compared to the amorphous- (a-) $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ deposited at 1 J/cm^2 . The tail-like absorption down to $\sim 3.5 \text{ eV}$ in the poly- $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ thin films did not change with PO_2 varied from 1 to 4 Pa, indicating that the tail-like absorption came not from oxygen deficiency but from the inherent structural property of the polycrystalline film such as nanocrystals and grain boundaries.

Next, we compared electrical properties of a- $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ and poly- $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$. As seen in Fig. 1(a), the poly- $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ thin film was deposited at the high laser fluence of 4.5 J/cm^2 , while the a- $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ film was deposited at 1.0 J/cm^2 (the other parameters such as the target–substrate distance of 40 mm and PO_2 of 4Pa were the same for both cases). Further, both of them were annealed at 200°C in vacuum, which improved their electrical properties due partly to reduction of excess/weakly-bonded oxygen [18]. As shown in Fig. 2(a), the Hall mobility (μ_e) at 300 K for the a- $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ ($6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) is doubly larger than that of the poly- $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ ($3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). The activation energy of μ_e is larger for the poly- $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ (45 meV) than that for the a- $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ (29 meV). The prefactors of

the Arrhenius plots were very similar, $\mu_0 = \sim 18$ and $\sim 17 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the $\text{a}-(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ and the $\text{poly}-(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ thin films, respectively. These results indicate that the extended mobility (μ_0 , i.e., mobility in single-crystallite or in single-domain within potential barriers) is not affected by the amorphous structure, which is similar to other AOSs including a-IGZO [1,19], and the Hall mobilities are determined by the electron transport potential barriers in CB (probably due to grain boundaries for the polycrystalline film and disordered structure for the amorphous film as reported in [19]). The carrier densities (N_e) at 300K were $\sim 2 \times 10^{17} \text{ cm}^{-3}$ and $\sim 4 \times 10^{17} \text{ cm}^{-3}$ for $\text{a}-(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ and $\text{poly}-(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$, respectively (Fig. 2(b)). Their activation energies were very similar ($\sim 43 \text{ meV}$), indicating that the donor levels are located at $\sim 0.09 \text{ eV}$ from the CBM. While,

3.2 Effects of chemical composition on $\text{a}-(\text{Ga}_{1-x}\text{Zn}_x)\text{O}_y$

Further, we investigated Ga-rich region in the $\text{a}-(\text{Ga}_{1-x}\text{Zn}_x)\text{O}_y$ system. Figure 3 shows XRD patterns of as-deposited $\text{a}-(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$, $\text{a}-(\text{Ga}_{0.70}\text{Zn}_{0.30})\text{O}_y$, and $\text{a-Ga}_2\text{O}_3$ thin films. Only halos from the $\text{a}-(\text{Ga}_{1-x}\text{Zn}_x)\text{O}_y$ films and the silica glass substrates were observed, substantiating that all the films were amorphous. Figure 4 compares optical properties for different Ga contents, from which E_g values were extracted from Tauc' plots (Fig. 4(b)) (note that $E_g = 3.37 \text{ eV}$ of ZnO is taken from [23] because Tauc' plot is not applied to a crystalline material.). E_g increased

with increase in the Ga content from 3.37 eV for crystalline ZnO, 3.47 eV for a-(Ga_{0.35}Zn_{0.65})O_y, 3.78 eV for a-(Ga_{0.70}Zn_{0.30})O_y, and to 4.12 eV for a-Ga₂O₃. To investigate how electronic structure changes by the incorporation of Ga, we measured energy levels by UPS and compare them in Fig. 5. It is seen that the change in E_g results mostly from the change in I_p (corresponding to the VBM level). On the other hand, the CBM levels almost unchanged from pure ZnO to pure Ga₂O₃, implying that their lowest unoccupied levels and the CB widths are similar.

Here, we like to discuss why the a-Ga₂O₃ has the deepest VBM level (i.e., the largest I_p). There would be several origins that affect the VBM and the CBM levels as follows. (i) It is known that the electronic levels in cations are raised by negative Madelung potential (MP) formed by surrounding anions and vice versa, which forms an open and large bandgap in ionic materials [24]; therefore, larger MP (e.g. by shorter interionic distances and larger ion charges) deepens the VBM level and raises the CBM level. Shortening interionic distances would have two effects. (ii) One is to increase the overlap of relevant atomic orbitals between adjacent cations and anions. It increases the energy splitting between the bonding orbitals and the anti-bonding ones, which deepens the VBM level and raises the CBM level. (iii) On the other hand, it would have an opposite effect; shorter interionic distance increases the overlap between ion orbitals in the CB-constituting cations and in the VB-constituting oxygens, and increases the

CB and VB band dispersions and widths, which raises the VBM level and deepens the CBM level. (iv) It is also pointed that anion p – cation d interaction is important; i.e., the VBM of II-VI compound semiconductor is raised by strong anion p – cation d anti-bonding coupling [25].

The data for crystalline oxides in Fig. 5 indicates that the VBM level becomes deeper in the order of ZnO, In_2O_3 , SnO_2 , and $\beta\text{-Ga}_2\text{O}_3$ although the VBM values have some distribution in reported values (the distribution ranges are shown by the pink regions). It is not explained simply by the ion charges because the VBM level of $\beta\text{-Ga}^{3+}_2\text{O}^{2-}_3$ is ~ 1 eV deeper than that of $\text{In}^{3+}_2\text{O}^{2-}_3$ although their formal ion charges are the same. As the Ga–O distances in $\beta\text{-Ga}_2\text{O}_3$ (0.180 – 0.208 nm) are smaller than the In–O ones in In_2O_3 (0.211 – 0.221 nm), it would be reasonable that the MP in In_2O_3 is smaller and the VBM is shallower than those in $\beta\text{-Ga}_2\text{O}_3$; however, the VBM level of SnO_2 is shallower than that of $\beta\text{-Ga}_2\text{O}_3$ although the MP of $\text{Sn}^{4+}\text{O}^{2-}_2$ should be larger than that of $\beta\text{-Ga}^{3+}_2\text{O}^{2-}_3$. If we consider the p – d coupling effect of the above origin (iv), it can explain the order of the VBM levels from ZnO, In_2O_3 , to [$\beta\text{-Ga}_2\text{O}_3$, SnO_2] because the d orbital levels deepens and becomes apart from O $2p$ in the order of Zn $3d$, In $4d$, Ga $3d$, and Sn $4d$ [26]. It is, however, difficult to explain the similar VBM levels between $\beta\text{-Ga}_2\text{O}_3$ and SnO_2 . The shorter Ga–O distances in $\beta\text{-Ga}_2\text{O}_3$ (0.180 – 0.208 nm) than the Sn–O ones in SnO_2 (0.203 – 0.204 nm) would contribute to deepening the VBM level of $\beta\text{-Ga}_2\text{O}_3$.

Finally, we should say that the VBM levels of these oxides would be affected by the above

several factors, and the relatively deep Ga 3d level and the short Ga–O distances form the deep VBM compared to ZnO and In₂O₃, respectively. The VBM level of a-Ga₂O₃ is shallower than that of β -Ga₂O₃, which would be explained that the disordered structure in a-Ga₂O₃ causes more distribution in the O 2p levels and raises the VBM level, as reported for a-IGZO [27].

Figure 6 compares carrier transport between the Zn-rich a-(Ga_{0.35}Zn_{0.65})O_y and the Ga-rich a-(Ga_{0.70}Zn_{0.30})O_y films. The μ_e values at 300 K are similar, 6 cm²V⁻¹s⁻¹ and 7 cm²V⁻¹s⁻¹ for the a-(Ga_{0.35}Zn_{0.65})O_y and the a-(Ga_{0.70}Zn_{0.30})O_y films, respectively (Fig. 6(a)). While, their carrier densities are different largely; i.e., $\sim 2 \times 10^{17}$ cm⁻³ and $\sim 4 \times 10^{15}$ cm⁻³ for the a-(Ga_{0.35}Zn_{0.65})O_y and the a-(Ga_{0.70}Zn_{0.30})O_y, respectively. As the prefactors of the Arrhenius plot (n_0) are close to each other ($n_0 = 1.04 \times 10^{18}$ and 1.49×10^{18} cm⁻³ for the a-(Ga_{0.35}Zn_{0.65})O_y and a-(Ga_{0.70}Zn_{0.30})O_y, respectively), the total donor densities would be similar. This difference is, therefore, associated with different donor levels (E_D) because E_D of the a-(Ga_{0.35}Zn_{0.65})O_y and the a-(Ga_{0.70}Zn_{0.30})O_y are different largely, 0.08 and 0.32 eV, respectively (estimated from the E_a values of 0.04 and 0.16 eV by $E_D = 2E_a$). In this (Ga_{1-x}Zn_x)O_y system, plausible donor sources would be oxygen deficiency and hydrogen [28]. As the CBM level is almost the same for these materials as seen in Fig. 5, the different E_D indicates the ionization levels of these donors depend largely on the chemical composition and/or local coordination structure of the donor; in other words, the universal donor level as reported for hydrogen donor [29] would not be applied to the

(Ga_{1-x}Zn_x)O_y system. As seen in Fig. 5, the difference in the VBM levels is 0.28 eV and close to the difference in E_D (0.24 eV), it appears that E_D is more likely aligned to the VBM level.

Summary

We deposited amorphous (Ga_{1-x}Zn_x)O_y films and discussed their structures, electron transport properties, electronic structures, and donor levels. We found that low laser fluences and low deposition rates are required to form amorphous films. The largely tuned band gap from 3.47 to 4.12 eV for $x = 0.65 - 0$ is determined almost solely by the valence band maximum level. It was also found that the donor levels from the vacuum level are largely dependent on the Ga content and appear to align better to the valence band maximum levels.

The large band gap of Ga-rich a-(Ga_{1-x}Zn_x)O_y would be applied to deep ultraviolet optoelectronic / photonic devices. This feature would also be interesting for thin-film transistors and other electronic devices that do not show light-induced degradation/light response in the visible-to-ultraviolet region. As a-(Ga_{1-x}Zn_x)O_y films are fabricated at room temperature and have flexible tunability of the band gap and the valence band maximum level, they would be applicable to designed hole blocking layers in flexible optoelectronic devices [30,31].

Acknowledgements

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) through Element Strategy Initiative to Form Core Research Center. J. Kim was supported by ACCEL Project sponsored by Japan Science and Technology Agency (JST). H. Hiramatsu was also supported by the Japan Society for the Promotion of Science (JSPS) through a Grant-in-Aid for Scientific Research on Innovative Areas "Nano Informatics" Grant Number 25106007, and Support for Tokyotech Advanced Research (STAR).

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Table 1. Relationship among deposition condition, film density, and chemical composition ratio for $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ thin films.

Laser fluence	Pulse repetition	Deposition rate	Film	Film density	Zn: Ga
(J/cm^2)	(Hz)	(nm/min)	thickness	(g/cm^3)	
			(nm)		
1.0	10	7.2	107.1	5.27	64.7: 35.3
1.5	10	9.8	110.2	5.33	64.5: 35.5
3.0	10	26.3	115.4	5.50	64.3: 35.7
4.5	10	34.8	117.1	5.69	65.2: 34.8

Figure captions

Fig. 1. Structures of $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ thin films. XRD patterns of (a) as-deposited thin films deposited at laser fluences between 1.0 and 4.5 J/cm². (Vertical bars show diffraction peak positions for 10-10_{ZnO}, 0002_{ZnO}, and 111_{β-Ga₂O₃}) and (b) annealed thin films, deposited at laser fluence 1.0 J/cm², at $T_a = 200\text{--}600$ °C. (c) TDS spectra for $m/z = 18$ (H₂O) of thin films deposited at laser fluences of 1.0 and 4.5 J/cm². (d) Optical absorption spectra of thin films deposited at fluences of 1.0 and 4.5 J/cm² and $P\text{O}_2 = 1\text{--}4$ Pa. That of crystalline ZnO is shown for comparison.

Fig. 2. Temperature dependence of (a) μ_e and (b) n_e for a- $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ and poly- $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ thin films.

Fig. 3. XRD patterns of as-deposited a- $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$, a- $(\text{Ga}_{0.70}\text{Zn}_{0.30})\text{O}_y$, and a-Ga₂O₃ thin films.

Fig. 4. Optical absorption spectra of as-deposited a- $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$, a- $(\text{Ga}_{0.70}\text{Zn}_{0.30})\text{O}_y$, and a-Ga₂O₃ thin films plotted in (a) logarithmic scale and (b) Tauc' plot.

Fig. 5. Band alignment of crystalline ZnO [10,21], a-(Ga_{0.35}Zn_{0.65})O_y, a-(Ga_{0.70}Zn_{0.30})O_y, and a-Ga₂O₃. Those for crystalline β-Ga₂O₃ [20], SnO₂ [21], In₂O₃ [21], and a-IGZO [22] are also shown for comparison, where the pink regions in I_p and the green regions in χ show the variation of reported values possibly caused e.g. by fabrication / treatment conditions, etc.

Fig. 6. Temperature dependences of (a) μ_e and (b) n_e for a-(Ga_{0.35}Zn_{0.65})O_y and (Ga_{0.70}Zn_{0.30})O_y thin films

Table 1. Relationship among deposition condition, film density, and chemical composition ratio for $(\text{Ga}_{0.35}\text{Zn}_{0.65})\text{O}_y$ thin films.

Laser fluence	Pulse repetition	Deposition rate	Film	Film density	Zn: Ga
(J/cm ²)	(Hz)	(nm/min)	thickness	(g/cm ³)	
			(nm)		
1.0	10	7.2	107.1	5.27	64.7: 35.3
1.5	10	9.8	110.2	5.33	64.5: 35.5
3.0	10	26.3	115.4	5.50	64.3: 35.7
4.5	10	34.8	117.1	5.69	65.2: 34.8

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6