An insight into doping mechanism in Sn-F co-doped transparent conducting ZnO films by correlating structural, electrical and optical properties

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Abstract

On the face of massively growing market of transparent optoelectronics, developing ZnO-based transparent conductive thin films as a promising substitute for indium-free transparent electrode is extremely important. However, the detailed function of the dopants, especially co-dopants acting on the electrical and optical properties of ZnO-based transparent conductive thin films is not clear yet. We present a detailed comparative investigation on the structural, electrical and optical properties of pulsed laser deposited ZnO thin films co-doped with Sn and F for the first time. An unexpected expansion in the lattice structure has been observed when Zn^{2+} are replaced by Sn^{4+} having smaller ionic radius. Electrical measurements show that there is no anticipated change in the carrier concentration with the dopant concentration. A minimum resistivity of 2.56×10^{-3} Ohm-cm with a carrier concentration of $4.41 \times 10^{20} \text{ cm}^{-3}$ has been obtained for 1 at% each Sn-F co-doped film. Most interestingly, a significant improvement in the ultraviolet (UV)/visible (VIS) photoluminescence peak intensity in Sn doped and Sn-F co-doped films in correlation with the structural and electrical properties allows us to propose that Sn doping into ZnO lattice causes a screening of the native Zn vacancy defects. While the presence of F co-dopant induces Sn^{2+} to occupy the lattice sites, as evidenced from the lattice expansion, an insignificant increase in the carrier concentration as well as enhanced UV emission of the co-doped films. The results obtained in this study shed light on the development of ZnO-based transparent electrodes.

Keywords: Pulsed laser deposition; Transparent conducting oxide; Sn-F co-doped ZnO; Carrier concentration; Photoluminescence; Native defects.

1. Introduction

There is an great importance of transparent conducting oxide (TCO) thin films for different optoelectronic devices such as thin film solar cells [1,2], flat panel liquid crystal displays, light emitting diodes [3,4] etc. The most commonly used TCO in transparent electronics is Sn doped In_2O_3 (ITO), where carrier density of more than $\sim 10^{21} \text{ cm}^{-3}$ and resistivity of $\sim 10^{-5} \text{ ohm-cm}$ have been achieved. Since In is relatively a scarce, and consequently an expensive metal, there is an urge to find the alternatives of ITO which will be able to bring in the comparable efficiency in those applications. Among the possible alternatives, doped ZnO thin film is a promising one because of its direct and wide band gap ($E_g = 3.37 \text{ eV}$ at room temperature), non-toxicity, high melting point (1975°C), low-price, abundance and most importantly, durability against hydrogen plasma which is used during solar cell fabrication [5,6]. There are numerous reports wherein various cations such as Al, Ga, B, In, Sn, Ti as well as anions like F, Cl have been doped into ZnO matrix to improve the conductivity. Most of these studies have been carried out to increase the number of free carriers in ZnO thin films by doping with trivalent cations like Al^{3+} , Ga^{3+} etc. The optimum impurity doping level for the highest carrier concentration was found to be varied within 1–3 at% for Al [7-13] beyond which the conductivity values deteriorate due to formation of excess crystal defects [9,10,14]. Similarly, transparent and highly conducting Ga doped ZnO has been obtained when optimum doping concentration of Ga_2O_3 varies from 2–5 wt % [15-18]. To enhance the conductivity, it is quite reasonable to dope ZnO with Sn^{4+} (TZO) because of the comparable ionic radius (69 pm for Sn^{4+} , and 74 pm for Zn^{2+}) [19,20] and tetravalency [21-25]. For instance, lowest resistivity of $2 \times 10^{-3} \text{ ohm-cm}$ has been obtained for pulsed laser deposited (PLD) TZO film containing 0.1 at.% Sn [22] while a resistivity of $8.32 \times 10^{-2} \text{ ohm-cm}$ have been reported for spray pyrolysis deposited TZO film containing six times Sn content of 0.6 at.% [26]. A lowest resistivity of $4.2 \times 10^{-2} \text{ ohm-cm}$ has been obtained when as high as 2.5 % Sn has been doped in ZnO film produced by a two stage dip coating method [27]. A maximum carrier concentration of $1.73 \times 10^{20} \text{ cm}^{-3}$ has also been reported for 10% Sn doped ZnO film deposited by chemical spray pyrolysis technique [28]. Therefore, process of Sn doping in ZnO changes the electrical property quite curiously.

Unlike Al and other trivalent and tetravalent cations, effect of F doping in ZnO (FZO) is less focused. Due to compatibility in the ionic radius of F^- (131 pm), with that of O^{2-} (138 pm) [29,30], F can easily be introduced into ZnO lattice by substituting O atoms. A film resistivity of $4.83 \times 10^{-4} \text{ Ohm-cm}$ has been obtained for PLD ZnO film containing 1 at% ZnF_2 [29] while a lowest resistivity of $6.53 \times 10^{-2} \text{ ohm-cm}$ has been obtained for chemical vapor deposited ZnO film with 0.48 at% F [31]. Zhang et. al have reported a lowest resistivity of $7.66 \times 10^{-2} \text{ Ohm-cm}$ for 3% F doped ZnO thin film prepared by magnetron sputtering [32] and In contrast, a lowest resistivity of 1 Ohm-cm has also been reported for 2 at% F doped sol-gel ZnO thin film [33,34]. It is quite obvious from the above literature that, there is a large variation in the optimum dopant content for obtaining minimum resistivity in TZO and FZO films which clearly indicate that the doping mechanism is process dependent and quite complicated. S doping has

also been attempted to enhance the conductivity of ZnO [35]. So, unless the doping mechanism is understood clearly, development of efficient ZnO-based TCO cannot be developed.

Impurity doping definitely causes a structural change directly or indirectly in terms of defects which affects different physical properties. Since the photoluminescence (PL) property is a signature of the structural quality, a change in position of emission peaks as well as a change in the luminescence intensity is an indication that the samples have gone through a tremendous structural change. Especially, when ZnO mostly exhibits dominant visible peaks in its PL spectrum as a manifestation of its different in-gap defect states, the structural changes brought in by impurity doping can suitably be enlightened by the PL studies to support the electrical properties. Very few studies correlated so far the PL properties with the electrical properties and explored the doping mechanism of ZnO-based conducting films. Having all these in mind, in this paper, we have investigated the electrical and PL properties of Sn and Sn-F co-doped pulsed laser deposited (PLD) ZnO films. An insightful mechanism of doping has been presented by analyzing the structural, absorbance, electrical, PL and X-ray photoelectron spectroscopy (XPS) data in details.

2. Experimental

The targets of doped and undoped ZnO were prepared by conventional ceramic method as described somewhere else [36]. To prepare the Sn-F co-doped target, high purity commercial ZnO (MERCK, 98% purity), Sn (SIGMA-ALDRICH, 99.8% purity) and NH_4F (MERCK, 99% purity) powders were mixed proportionately in an agate mortar for several hours and pressed them in the form of a pellet with a diameter of 1.5 cm under 5 ton pressure. Then the pellets were sintered at 1000 °C for 24 hours in a tubular furnace in ambient condition for solid state reaction. In order to understand the co-doping effect, singly F and Sn doped targets were also prepared. Films of thickness around 200 nm were deposited on properly cleaned glass substrates by ablating these sintered targets in a PLD system (Neocera) fitted with a KrF excimer laser (Coherent) with an emission wavelength of 248 nm, repetition rate 10 Hz, and energy 300 mJ in oxygen partial pressure 2.5 mTorr. The number of laser pulse used were 60000, base pressure was 5×10^{-5} Torr and the target to substrate distance was 10 cm. The substrate temperature was maintained at 300 °C. Doping contents and the sample names have been noted in table-I.

X-ray diffractometry (XRD; model: BRUKER D 8) with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation was used to characterize the crystal structure of the films. The surface morphology has been analyzed by a field-emission scanning electron microscopy (FESEM; JEOL model: JSM-6700F). The optical transmission spectra with a resolution of 1 nm were recorded using a UV-VIS-NIR spectrophotometer (model: Cary-5000, 200–3200 nm). The room temperature PL spectra with 1 nm resolution were measured by exciting the samples with a He–Cd laser (Kimmon Koha Co., Ltd.; model KR1801C) as 325 nm excitation source and recording the luminescence using a spectrometer (Horiba Jobin Yvon, Model: iHR 320) together with a photomultiplier tube. The

resistivity, carrier concentration, and mobility at room temperature were measured by the Hall measurements using four probe in Van der Pauw geometry with the help of HEMS (model: HMS 3000). X-ray Photoelectron Spectroscopy (XPS; Omicron, serial no: 0571) was studied to identify the elemental states.

3. Results and discussion

3.1 Structural properties

The XRD patterns of the films in Fig. 1 shows a sharp peak around 34.4° which corresponds to the (002) peak of the hexagonal wurtzite structure of ZnO. One and only highly intense (002) peak indicates that the films have been grown preferentially along c-axis. The magnified view of the peak positions as shown in the inset in Fig. 1 clearly shows that there is a shift towards lower 2θ values indicating that there is a slight expansion in the lattice which is also reported by Venkataraj et al. [37]. However, this is in contrast to the reports wherein a shift towards higher 2θ values has been found [22,24,38,39]. Since Sn^{4+} and F^- both are having ionic radii slightly lower than Zn^{2+} and O^{2-} respectively, it is expected that there would be a slight lattice contraction. Therefore, our result indicates that an unusual effect in the lattice has been occurred due to doping. The reason behind the slight lattice expansion is understood latter when XPS results have been analyzed. The FWHM values of the (002) peak are given in table-1. F doping increases the value notably, while Sn doping and Sn-F co-doping cause a slight increase in the value. An increase in the FWHM value for 10FZO film as compared to ZnO indicates probably a structural degradation due to defect formation.

In order to know and compare the microstructure of all the thin films, FESEM images have been shown in Fig. 2(a)-(d). The images show that the texture of the films is compact with mostly spherical shaped particles. The diameter of the particles as roughly estimated from the FESEM images for ZnO, 10FZO, 10TZO is in the range of 30-40 nm but for 10FTZO film, it is around 20-25 nm. The crystallite size has also been calculated using Scherrer formula and noted in Table -1 which shows that the values are quite close to those estimated from FESEM images. The result of 10FZO is at par with the observations made by Ilcan et al. [24] who have got grains of diameter 24-35 nm for sol-gel derived FZO thin film. A wide range for grain size of 10-80 nm for Sn doped ZnO grown using various techniques have been reported [40-42]. Energy Dispersive X-ray (EDAX) mapping has been done in order to know the distribution of the mother and dopants elements (Fig. 2(e)-(h)) in 10FTZO film and it is found that the dopants Sn and F are quite uniformly distributed in the observed area of the co-doped film.

3.2 Transmission properties

Fig. 3 shows the transmission spectra of all the films as a function of wavelength. All the films exhibit sharp band-edge absorption below 380 nm. ZnO and 10FZO films show high transparency (75%-90%) in the visible solar spectrum region i.e. from 400 to 800 nm.

However, the transmission value is lower (~50%) for the 10TZO and 10FTZO films. Relatively lower transmission value (70%-80%) has also been reported by Holmelund et al. and Chahmat et al. for only 0.05% and 2% Sn doped ZnO film respectively [21,43]. The lower transmission value in the films containing 1% Sn is probably due to light absorption in the film. It has been reported that a material having an element in two different oxidation states or in a mixed oxidation states shows abnormally deep and intense coloration due to electron transfer between the different oxidation states of the element causing intense light absorption which is termed as the interaction color [44-46]. A blue shift in the absorbance edge for the doped sample has been observed and magnified view is shown in the inset of Fig. 3. The optical band gap of undoped and doped films has been calculated from the Tauc plot as shown in Fig. 4 and values are given in the Table-2. Both F and Sn doping cause an increase in the band gap of ZnO while the change is much more in case of Sn doping as compared to F doping. The enhanced band gap has also been reported previously [25,27,47,48]. Pan et al. [39] also have found an increase in the band-gap from 3.21 eV for ZnO to 3.36 eV for 2% Sn and 3% F co-doped FTZO thin film. Burstein–Moss effect is mainly responsible for this kind of broadening (blue shifting) of the energy band [25,48]. The shifting of the band-gap further indicates that the carrier concentration increases which blocks the lowest state of the conduction band.

3.3 Electrical and photoluminescence properties

Table-2 further shows the values of carrier concentration, resistivity, and mobility for all the films. Due to F doping, the carrier concentration increases almost three times to that of ZnO and attains a resistivity value of 3×10^{-3} Ohm-cm. This value is lower than the value of 4.83×10^{-3} Ohm-cm as observed by Cao et al. [29] for PLD grown ZnO sample containing 1 at% ZnF₂. Unexpectedly, a low increase in the carrier concentration in FZO film is probably due to the structural defects as evidenced from the FWHM value of the (002) peak. Sn doping causes an increase in the carrier concentration by almost six times to that of ZnO. The resistivity value of 5×10^{-3} Ohm-cm for our 1% Sn doped (10TZO) film is much lower than the value of 4.2×10^{-2} Ohm-cm as reported by Vaezi et al. [27] for much higher Sn doping i.e 2.5%. The table shows that a maximum carrier concentration of $4.41 \times 10^{20} \text{ cm}^{-3}$ has been obtained for 10FTZO film with a resistivity value of 2.6×10^{-3} Ohm-cm. With even higher dopant concentration as compared to ours, Pan et al. [39] have obtained the best resistivity of only 1×10^{-3} ohm-cm for 2% Sn and 3% F co-doped ZnO thin film. The figure of merit (FOM) of the all the films has been calculated using the formula given below [49,50]

$$\text{FOM} (\varnothing_{\text{TM}}) = T^{10}/R_s$$

where T is the transmission at 550 nm and R_s is the sheet resistance. The FOM values are noted in Table-2. It is seen that in F doped ZnO film, the value is improved while in Sn doped it is degraded due to lower transmission value.

As a tetravalent cation, each Sn should donate two free electrons when it replaces one Zn cation and hence a large number of free carriers should be generated for 1 at% Sn doping. Our electrical data shows that there is only a six times and an order increase in the carrier concentration by Sn and Sn-F co-doping respectively. It has been reported that doping of ZnO by metallic cations may lead to charge density non-centrosymmetry [51]. Therefore, the existing literature data as well as our results suggest that some unusual phenomenon is occurring in the lattice. We assume that the mechanism of Sn doping is not straightforward. Therefore, to have an insight into the doping mechanism, besides the expected occupancy of Sn^{4+} at Zn sites, two other probabilities can be considered: (i) Sn^{2+} at Zn sites (this possibility occurs as the films are deposited comparatively at low O partial pressure) and (ii) Sn^{4+} at Zn sites causing some complex defect formation [37]. In both the cases, we should not expect an increase in the carrier concentration. However, a small increase in the free carrier concentration in our data indicates that few Zn^{2+} sites are certainly occupied by some Sn^{4+} . If it is the case, then a question arises naturally that what happens to the the rest of the Sn dopants which led us to examine the PL properties of the films since signature of defects is usually well reflected in the PL spectra. The PL spectra in Fig. 5 show a strong UV emission peak and a weak visible emission from 400–625 nm for all the films (the magnified view of the visible emission is shown in the inset in Fig.5). A blue shift in the UV peak maxima has been noted which is at par with the transmittance results. For 10FZO film, as O is being replaced by F, degradation of the UV peak intensity has been observed as compared to ZnO which is probably due to formation of some structural defects as also evidenced by the FWHM of the XRD peak. However, additional role of an increase of the linear electro-optic effect in F doped ZnO film cannot be ruled out as a cause [52]. For 10TZO and 10FTZO films, the UV intensity is enhanced as compared to that of ZnO film. The enhancement is at par with the results for 2% Sn-3% F co-doped and 1% Sn doped ZnO films reported by Pan et al. and Kumar et al. respectively [39,53]. However, their explanations behind the enhancement are quite vague. An enhancement in the UV peak intensity occurs only when radiative and/or non-radiative defect centers within the band gap are reduced. Green emission is the most notorious one affecting the intensity of the UV emission and the former being caused by the Zn vacancy (V_{Zn}) defects [54-57]. In our Sn doped films, some Sn^{4+} ions are probably causing charge compensation by making a complex with V_{Zn} [37]. This is apparently similar to a situation where the V_{Zn} defects are screened. Now, as V_{Zn} is assigned as a cause for the green emission in ZnO, due to engagement of V_{Zn} defects in complex formation with Sn^{4+} , logically, a reduced intensity of the green emission and an enhanced intensity of the UV emission are expected. This indeed has occurred and proved when we have calculated the UV/VIS (considering the visible emission at 500 nm) ratios for all the films. The values noted in Table-3 show that the ratio significantly decreases for 10FZO while it increases for 10TZO and 10FTZO as compared to ZnO. This indicates two aspects: only F dopant increases and only Sn dopant decreases (screens) the radiative defects while the presence of F along with Sn, further reduces/screens the defects (the inset in Fig. 5).

A strong correlation between the PL properties of the bulk pellets used for ablation and those of the films has been evidenced when the PL spectra (Fig. 6) of the former have been investigated. Surprisingly, it shows that 10FTZO pellet has the highest intensity of the green emission, and next are 5FTZO, 10TZO, 10FZO and ZnO pellets which is exactly the opposite trend obtained in case of the UV emission intensity in the films. This indicates that there is a contrast relation between the PL spectra of the bulk and the film. The O partial pressure was quite different during preparation of the bulk pellets and the films and formation of V_{Zn} defects is low under low O partial pressure during film deposition [58,59]. Therefore, the difference in the emission properties further strengthens the evidence that further due to screening of the V_{Zn} defects in Sn and F co-doped films, the green emission intensity is lower and the UV intensity is much higher in the films as compared to the bulk.

3.4 XPS elemental studies

Valence state of Sn in Sn and Sn-F doped films is confirmed from the XPS elemental Studies. A representative full scan of XPS spectrum of 10TZO has been shown in Fig. 7 which confirms the presence of Zn, O and Sn. The insets show the enlarged view of the O and Sn peaks. Fig. 8 shows the deconvoluted O signal from 10TZO film which consists of two peaks centered at 530.6 eV and 531.5 eV. The component on the lower binding energy side of the $O1s_{1/2}$ spectrum is attributed to O^{2-} ions within hexagonal wurtzite structure surrounded by Zn^{2+} (or the substituted Sn) [14,36]. The peak located at 531.5 eV at the higher binding energy side is normally attributed to the presence of loosely bound chemisorbed O on the surface of the films [14,36]. The $Sn3d_{5/2}$ peak has a clear shoulder at lower energy side and thus fitted to two peaks with centre at 486.7 eV and 485.3 eV as shown in Fig. 9. The higher energy peak corresponds to Sn^{4+} [60,61] and lower energy peak corresponds to Sn^0 . The energy difference of ~ 2.0 eV between Sn^{4+} and Sn^0 has been reported by many groups in SnO_2 [60,62]. It suggests that besides Sn^{4+} , Sn^0 is likely to be present in 10TZO film. However, unlike Sn^{4+} , Sn^0 probably sits in the interstitial position due to large mismatch of ionic radius. The XPS spectrum of 10FTZO films as shown in the Fig. 10 also confirms the presence of Zn, O and Sn. The insets show the enlarged view of $F1s$ [39] and $Sn3d$ peaks. Fig. 11 shows the XPS peak for $Sn3d_{5/2}$ can be fitted to two peaks one at 486.8 eV and 486.1 eV respectively for Sn^{4+} and Sn^{2+} in the 10FTZO films [60,61,63]. There is a difference of nearly 0.70 eV between Sn^{4+} and Sn^{2+} signal which has been earlier reported by many other groups [60,64]. Presence of Sn^{2+} has also been proposed in Sn doped ZnO films grown by PLD [37]. When larger Sn^{2+} ion occupies the Zn^{2+} site, the lattice should expand which has been supported by the XRD results but in such case, no increase in the carrier concentration is expected. The XPS results suggest that when Sn is doped, Sn^{4+} and Sn^0 are present and when Sn-F co-doping is done, Sn remains in Sn^{4+} and Sn^{2+} states. Thus comparing the two XPS results, it may be inferred that due to presence of more electronegative F ion (electronegativity of F is more than O), Sn^0 is converted to Sn^{2+} occupying V_{Zn} sites in 10FTZO film. This is also supported by the higher UV intensity as compared to the green one

indicating less radiative recombination via in-gap defects. Therefore, Sn doping in presence of F dopants, does optimally increase the carrier concentration and enhances the UV emission.

4. Summary

In summary, by studying and comparing the structural, electrical and optical properties of F, Sn and Sn-F co-doped PLD grown ZnO thin films, an insight into the Sn doping and Sn-F co-doping mechanism has been presented. The electrical properties have been nicely correlated with the PL and XPS data to reveal that certain Sn^{4+} dopants in the lattice remain complexed with V_{Zn} and in co-doped film; Sn^{2+} occupies V_{Zn} as a result of which the UV emission is enhanced and the carrier concentration does not increase beyond a certain dopant value. We believe that this knowledge would be very useful for further development of co-doped ZnO based TCOs for various optoelectronic devices.

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Figure Captions:

Fig. 1: X-ray diffraction patterns of a) ZnO, b) 10FZO, c) 10TZO, d) 5FTZO, e) 10FTZO films. Inset shows the enlarged view of the peak shift.

Fig. 2: FESEM images of a) ZnO, b) 10FZO, c) 10TZO, d) 10FTZO. EDAX mapping of elements (e) Zn, (f) O, (g) F, and (h) Sn.

Fig. 3: UV-VIS-NIR transmission spectra of a) ZnO, b) 10FZO, c) 10TZO, d) 5FTZO, e) 10FTZO films. Inset shows the shifting of band-edge absorption in 360 - 400 nm range.

Fig. 4: Tauc plot for a) ZnO, b) 10FZO, c) 10TZO, d) 5FTZO, e) 10FTZO films.

Fig. 5: The PL spectra of a) ZnO, b) 10FZO, c) 10TZO, d) 5FTZO, e) 10FTZO films. Inset shows the shifting in the PL peak position.

Fig. 6: The PL spectra of a) ZnO, b) 10FZO, c) 10TZO, d) 5FTZO, e) 10FTZO target pellets.

Fig. 7: XPS spectrum of 10TZO film. Upper left inset shows the enlarged O 1s signal and bottom right inset shows the enlarged Sn 3d signal.

Fig. 8: XPS spectrum showing experimental and theoretically fitted peaks corresponding to O 1s component of 10TZO film.

Fig. 9: XPS spectrum showing experimental and theoretically fitted peaks corresponding to Sn 3d_{5/2} component of 10TZO film.

Fig. 10: XPS spectrum of 10FTZO film. Upper left inset shows the enlarged F 1s signal and bottom right inset shows the enlarged Sn 3d signal.

Fig. 11: XPS spectrum showing experimental and theoretically fitted peaks corresponding to Sn 3d_{5/2} component of 10FTZO film.

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Graphical Abstract:

Table – 1: Content and doping element, sample name, FWHM of the (002) XRD peak and Grain size.

Content and doping element	Sample name	FWHM (degree)	Grain Size (nm)
None	ZnO	0.28	30
1 at% F	10FZO	0.36	23
1 at% Sn	10TZO	0.31	28
0.5 at% F and Sn	5FTZO	0.29	29
1.0 at% F and Sn	10FTZO	0.31	27

Table – 2: Band-gap, carrier concentration, resistivity and mobility and FOM values of ZnO, doped and co-doped films.

Sample	Band-gap (eV)	Carrier Concentration (cm^{-3})	Resistivity ($\Omega\text{-cm}$)	Mobility ($\text{cm}^2/\text{V.s}$)	FOM (Ω^{-1})(10^{-4})
ZnO	3.23	4.84×10^{19}	6.79×10^{-3}	18.97	1.26
10FZO	3.25	1.42×10^{20}	3.00×10^{-3}	14.83	2.90
10TZO	3.37	2.72×10^{20}	5.06×10^{-3}	4.53	0.07
5FTZO	3.29	1.19×10^{20}	6.24×10^{-3}	8.41	1.43
10FTZO	3.36	4.41×10^{20}	2.56×10^{-3}	5.49	0.13

Table – 3: UV/VIS PL ratio of the films.

Sample Name	UV/VIS
ZnO	4.8
10FZO	1.9
10TZO	6.5
5FTZO	3.0
10FTZO	10.7

Fig. 1

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Fig. 2

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Fig. 3

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Fig. 4

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Fig. 5

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Fig. 6

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Fig. 8

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Fig. 9

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Fig. 10

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Fig. 11

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