Aromatic-doped Boron Carbide Films Formed by PECVD of Metacarborane and Aniline or Pyridine: Chemical and Electronic Structure

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Aromatic-doped Boron Carbide Films Formed by PECVD of Metacarborane and Aniline or Pyridine: Chemical and Electronic Structure

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Abstract

Closo- 1, 7-dicarbadoecaborane (metacarborane) and aniline or pyridine have been used to fabricate semiconducting composite films by plasma enhanced chemical vapor deposition (PECVD). Chemical and electronic structures of films with aniline/metacarborane or pyridine/metacarborane ratios of ~3:1 were characterized by x-ray photoelectron spectroscopy (XPS), variable angle spectroscopic ellipsometry (VASE), and first-principles density functional theory (DFT)-based electronic structure calculations. Aniline moieties are coordinated to carborane icosahedra by C-B bond formation, whereas N-B and possibly C-B bonding was observed for pyridine/metacarborane films. The aniline/metacarborane film displayed indirect and direct band gaps of 1.0 eV and 2.9 eV, respectively, with corresponding values for the pyridine/metacarborane film of 1.4 eV and 3.3 eV. In contrast, the metacarborane film without aromatic doping exhibits indirect and direct band gaps of 2.6 and 4.9 eV, respectively. DFT results indicate that in both aniline/metacarborane and pyridine/metacarborane film, states near the valence band maximum are associated with the aromatic species, while states near the bottom of the conduction band are associated with either the aromatic or metacarborane moiety. These results indicate that aromatically-doped boron carbide films derived from metacarborane isomers exhibit very similar structures and characteristics to those formed by orthocarborane isomers. Due to the n-type (p-type) nature of boron carbide films formed by PECVD metacarborane (orthocarborane), the results reported here suggest that aromatic doped boron carbide p-n junctions are possible for neutron detection or other applications.

Keywords

Boron carbide; PECVD; band gap; HOMO-LUMO gap

I. Introduction

Semiconducting composite films derived from closo-1, 2-dicarbadoodecaborane (orthocarborane) or closo- 1, 7-dicarbadoodecaborane (metacarborane) are of long-standing interest for neutron detection applications [1–9]. Metacarborane or orthocarborane-derived boron carbide films are n-type or p-type, respectively [10], and the formation of p-n junctions from these films to increase detector sensitivity has been demonstrated [1]. Such films, however, are generally poor semiconductors, exhibiting inconsistent and often defect-dominated electronic characteristics, including carrier lifetime and current-voltage characteristics [11,12] and mobility [13]. Recently, however, aromatically-doped boron carbides, consisting of films formed by the PECVD codeposition of orthocarborane with pyridine or aniline have been reported [8,14–16]. Such films, with aromatic/orthocarborane ratios from $\sim 2:1$ to $> 10:1$, exhibit significantly reduced indirect and direct band gaps relative to PECVD films without aromatic doping [7,17]. PECVD pyridine/orthocarborane films have recently been shown to also exhibit an order of magnitude increase in charge carrier lifetime and enhanced electron-hole separation relative to films without pyridine [7], as well as an 850% increase in charge generation on a per B atom basis [8,14]. Such results suggest the attempt to make analogous aromatic/metacarborane films as a first step towards the potential formation of both p-type and n-type aromatic-doped boron films for p-n junctions in applications such as neutron detection or photocatalysis [18]. We report here the formation and general structural/electronic characterization of films formed from PECVD of aniline or pyridine with metacarborane.

II. Experiment

Films were fabricated by PECVD co-deposition of metacarborane and pyridine or aniline in a 70 mTorr Ar inductively-coupled plasma (20 W) onto Si (100) substrates. The detailed procedures and plasma conditions are described elsewhere [16]. Film deposition was carried out

in a vacuum deposition chamber (base pressure 1×10^{-7} Torr) and analysis in an ultra-high vacuum chamber (base pressure 2×10^{-10} Torr) with capability of x-ray photoemission spectroscopy (XPS). Sample transport between chambers was accomplished under controlled vacuum conditions using a linear feedthrough. XPS spectra were acquired with a 140 mm mean radius hemispherical analyzer with channel plate detector, operated in a constant pass energy (23.5 eV) and Al K α radiation from an unmonochromatized source. Si (100) substrates were cleaned prior to CVD by Ar ion bombardment (1 keV).

Aniline/metacarborane or pyridine/metacarborane ratios were controlled by the flow rates of precursors. Metacarborane mass flow rate was maintained at 5 sccm (standard cubic centimeter per minute). In this experiment, aniline or pyridine flow rates were also set at 5 sccm, yielding aromatic/metacarborane ratios of ~3:1.

Analysis of photoemission spectra was carried out by methods described previously [17,19,20]. Binding energies for XPS were corrected by setting the substrate Si (2p) peak binding energy at 99.3 eV [21]. Deconvolution of B 1s, C 1s and N 1s spectra were accomplished by fitting the experimental spectra with Gaussian-Lorentzian peaks with FWHM of 1.5 eV, 1.4 eV and 1.8 eV, respectively, based on previous experiments [17,19]. Relative aromatic/metacarborane stoichiometry was determined from relative N 1s/B 1s XPS- intensity derived concentration ratios, assuming that both aromatic and carborane precursors remained intact during the deposition process. This assumption has been previously verified for PECVD aniline/orthocarborane and pyridine/orthocarborane films [17]. In order to verify this for aniline/metacarborane films and pyridine/metacarborane films experimentally-derived atomic concentration ratios based on B 1s, C 1s and N 1s XPS intensities were compared to corresponding calculated ratios assuming that aromatic and metacarborane precursors remain

essentially intact during PECVD (Supplemental information, Table SI.). The close agreement between experimental and calculated XPS intensities indicate that, as for aromatic/orthocarborane films deposited under very similar plasma conditions [17], both aromatic and metacarborane moieties remain essentially intact under the PECVD conditions used in these experiments.

Experimental B/C atomic ratios (see supplemental information, Table SI) are close to, but consistently smaller than corresponding calculated ratios. This may reflect the presence of a small amount of extra-icosahedral carbon. Previous studies [22] have established that such carbon may be present in varying amounts, depending upon plasma deposition conditions.

The typical sampling depth of core level photoemission is limited to $\sim 50 \text{ \AA} - 100 \text{ \AA}$ [21]. Since film thicknesses determined from VASE data (see below) were significantly greater, XPS data were acquired periodically during the film deposition process. No significant changes in XPS-derived stoichiometries were observed for these films over the course of the deposition process, indicating generally uniform film composition.

Density functional theory (DFT) calculations within the Generalized Gradient Approximation (GGA) were performed using Gaussian 09 software with the B3LYP hybrid functional and 6-31 ++ 2d 2p basis set [23]. Total energy and electronic structures, including the valence and conduction band densities of states, were extracted from fully relaxed structures by assigning Gaussians of 1.0 eV FWHM to each eigenvalue [23,24].

In order to determine the relative stability of aniline (or pyridine) bonding to a metacarborane B site via the aniline (pyridine) N or ring C site, the total energies of each relaxed bonding configuration were compared. The relative stability of two structures can in

general be evaluated by the energy difference of the fully relaxed structures based on the definition of formation energy [25]:

$$(1) \quad \Delta E = E_{total}^2 - E_{total}^1 - \sum_i n_i \mu_i + Q(E_F + E_{VBM})$$

where E_{total} is the total energy, n_i is the number difference of atom type i between structure 1 and 2, μ_i is the chemical potential of atom i . In all cases dealt with here, the last term in (1) is zero, because we are dealing with neutral systems. Of interest here, however, are the relative energies of aniline/metacarborane or pyridine/metacarborane isomorphs, in which only the relative energies of, e.g., N-B vs C-B bonding configurations are examined for aniline/metacarborane or pyridine/carborane interactions. The third term in (1) is also zero for aniline/metacarborane isomorphs through N-B vs C-B, whereas there is one hydrogen atom difference between N-B and C-B bonding configurations for pyridine/metacarborane bimolecular cluster. The total energy of H_2 is -32.396 eV. Therefore, the calculated total energies discussed here may be compared for different isomers, but not, e.g., for an aniline-metacarborane vs pyridine-metacarborane structure.

FTIR spectra were acquired ex-situ using a Bruker Vector 22 spectrometer in transmission mode, with films deposited on Si (100) substrate [16].

Experimental band gap measurements were carried out by VASE, using films deposited on n-Si (100) substrates, over a range of photon energies in the visible to ultra-violet range (1.0 eV – 4.5 eV), in increments of 0.02 eV, at angles of incidence from 45^0 to 55^0 , in 5^0 increments. Data were fit by standard methods [26,27], using commercially available software. Standard spectroscopic ellipsometry determines the ratio (ρ) of the complex-valued Fresnel reflection coefficients r_p and r_s and is commonly presented by parameters ψ and Δ where $\rho = r_p/r_s = \tan(\psi)e^{i\Delta}$.

The absorption coefficient α was determined as a function of energy by the Cauchy model [26,27] fitted to experimental data. Indirect band gap and direct band gap were determined by Tauc plot [26]. In the case of inter-band transitions, the optical band gap energy E_g is calculated by the following relationship [26]:

$$\alpha^N = C(h\nu - E_g)$$

in which C is the fitting constant, and $N=1/3$ or 2 for forbidden indirect band or allowed direct band to band transitions, respectively.

III. Results

III.-A. XPS

Core level XPS spectra for PECVD composite films formed from pyridine/metacarborane, aniline/metacarborane and pure metacarborane are shown in Fig. 1. B 1s, C 1s and N 1s spectra are displayed in Fig. 1a-c, respectively, for a film with a pyridine/metacarborane ratio of ~3:1. Corresponding spectra for a PECVD aniline/metacarborane film with aniline/metacarborane ratio of ~3:1 are shown in Fig. 1 d-f. B 1s and C 1s spectra for a PECVD metacarborane film without aniline or pyridine are shown in Figs. 1 g and h.

The B 1s spectrum for the pure metacarborane film (Fig. 1 g) can be fit with three components corresponding to $B^2-\underline{B}$, $B-\underline{B}-C$ and $C-\underline{B}-C$, corresponding to B bonds to 0, 1 or 2 C nearest neighbors, with respective binding energies at 188.4 eV, 189.2 eV and 189.9 eV [19,23]. The three features exhibit relative intensities with a ratio of 2:6:2, different from the same three components in pure orthocarborane of 4:4:2 [19]. Importantly, the C 1s spectrum for this film (Fig. 1 h) exhibits significant intensity near 284 eV binding energy, attributable to C in an icosahedral environment, but not at the lower binding energies observed for aromatic-free PECVD orthocarborane-derived films, and attributable to C in extra-icosahedral environments,

such as bridging between icosahedra [20]. Whether this difference is due to small differences in plasma deposition conditions, or to some other factor, cannot be determined from this data. The B 1s and C 1s spectra for the PECVD metacarborane film, however, are consistent with B-B bonding between icosahedra.

In comparison with B 1s spectrum for the pure metacarborane film, the B 1s spectrum for the aniline/metacarborane film (Fig. 1 d) is observed to shift to higher binding energy, near 190 eV. This shift, however, is not as large as that exhibited by the B 1s spectrum for the pyridine/metacarborane film, near 191 eV (Fig. 1 a). Since both shifts indicate B bonding to more electronegative C or N atoms, the larger shift in the pyridine/metacarborane film is attributed to B-N bond formation, while the smaller shift in the aniline/metacarborane B 1s spectrum indicates bonding between ring C atoms and icosahedral B atoms, without N-B bond formation. Additionally, the broad nature of the B 1s spectrum for the pyridine/metacarborane film indicates that pyridine coordination via ring C bonding to icosahedral B sites may also occur. Similar effects regarding the absence or presence of N-B bond formation have been observed for pyridine/orthocarborane and aniline orthocarborane films [16,17], and for PECVD orthocarborane films with electron-induced B-NH₂ bond formation in the presence of NH₃ [28]. This findings are also corroborated by two dominant features of the N 1s spectrum for pyridine/metacarborane (Fig. 1 c). The N 1s spectrum can be fit with features corresponding to N-C and N⁺ with respective binding energies at 399.5 eV and 401.3 eV [29]. The N 1s feature at lower binding energy is consistent with N in the pyridine ring, while the feature at higher binding energy is attributable to the formation of tetrahedrally coordinated, cationic N⁺ formation [29]. In contrast, the N 1s spectrum for aniline/metacarborane (Fig. 1 f) exhibits only one prominent feature, near 399.5 eV, which is consistent with N atoms in the bonding environment for

polymerized aniline [29]. Thus, the data in Fig. 1 indicate that the N site in aniline is not involved in bonding to metacarborane, but that pyridine N sites are involved, and pyridine C sites may also be involved.

Total energy calculations were carried out to understand whether C_R-B (C_R : aromatic C) bonding or $N-B$ bonding between icosahedra and aromatics is energetically favored. Aniline/metacarborane bimolecular clusters exhibiting $N-B$ or C_R-B bonding are shown in Fig. 2 a and b, respectively. Corresponding pyridine/metacarborane bimolecular clusters are shown in Fig. 2 c, d. A bi-metacarborane cluster exhibiting B-B bonding is shown in Fig. 2 e. Calculated total energies and energy differences are summarized in Table. I for the aniline-metacarborane and pyridine-metacarborane bimolecular clusters. In the aniline/metacarborane case, the bimolecular cluster with C_R-B bond formation is 0.272 eV lower than the structure with N-B bond formation. For the pyridine/metacarborane bimolecular cluster, the N-B structure is lower by 0.075 eV. Therefore, the summarized results indicate that for aniline/metacarborane, C_R-B bond formation between icosahedron and aniline is energetically significantly favored relative to N-B bond formation; while in pyridine/metacarborane film, N-B bond linkage is energetically favored, but only by a much smaller amount. These findings corroborate the experimental XPS evidence (Fig. 1) and parallel results for analogous films formed with orthocarborane [16].

III.-B. Calculated Densities of States

DFT cluster calculations were carried out for bimolecular clusters incorporating the basic features of the XPS results, as shown in Fig. 2. These include a metacarborane/aniline bimolecular cluster with B-C bonding (Fig. 2 b), a metacarborane/pyridine bimolecular cluster incorporating B-N bonding (Fig. 2 c), and a metacarborane-metacarborane cluster with B-B bonding (Fig. 2 e). H atoms are not shown in Fig. 2 to make the molecular structures clear to

read. In reality, H atoms are removed from B sites where bonding is formed between aromatic groups and carborane in DFT calculations. The qualitative determination of the hydrogen content in the PECVD boron carbide films has been achieved by finding the area of B-B stretching mode ($\sim 1370\text{ cm}^{-1}$) [30] and the B-H stretching mode ($\sim 2580\text{ cm}^{-1}$) [31] in PECVD orthocarborane and metacarborane films in Fig. S1 (Supplemental information, Fig. S1). A comparison of B-H/B-B intensity ratio for both films is shown in Table. II. The good agreement of the B-H/B-B intensity ratios for the PECVD orthocarborane and metacarborane films (without aromatic content) indicates that these two films contain similar numbers of B-H bonds. For a more accurate assay of H content in the films, however, techniques such as nuclear reaction analysis must be employed [32].

Valence and conduction band densities of states (DOS) derived from DFT molecular orbital calculations for the bi-metacarborane cluster, pyridine/metacarborane bimolecular cluster with N-B bonding, and aniline/metacarborane bimolecular cluster with C-B bonding are shown in Fig. 3 a-c, respectively. Addition of aniline or pyridine results in extra density of states at the top of valence band in comparison with the bi-metacarborane cluster, which indicate that states near the top of valence band are of primarily aromatic character. Similar observations regarding the valence band DOS derived from experimental valence band photoemission have been reported for aromatic/orthocarborane films produced by electron beam-induced cross-linking [33] and for aromatic/orthocarborane films produced by PECVD [7,17]. The calculated HOMO-LUMO gaps for the bi-metacarborane cluster, as well as for the pyridine/metacarborane and aniline/metacarborane bimolecular clusters are listed in Table. III. The calculated HOMO-LUMO gap for aniline/metacarborane is 2.7 eV, for pyridine/metacarborane is 3.5 eV, and for bi-

metacarborane is 4.8 eV. Chemical bonding between carborane and aromatics results in narrower HOMO-LUMO gap, compared bonding between metacarborane icosahedra.

III.-C. Ellipsometry-determined Band Gaps

VASE was used to measure band gaps. The experimental curves of parameters ψ and Δ are shown fitted to a Cauchy model in Fig. 4. Plots of $\alpha^{1/3}$ (indirect band gap) and α^2 (direct band gap) vs. energy are shown in Fig. 5 a, b for a 3:1 PECVD aniline/metacarborane film, in Fig. 5 c, d for a PECVD 3:1 pyridine/metacarborane film, and in Fig. 5 e, f for a PECVD metacarborane film. VASE-derived indirect and direct band gap energies are listed in Table. III, in comparison to corresponding calculated HOMO-LUMO gaps. Composite films fabricated from aniline/metacarborane exhibit an indirect band gap of 1.0 eV and direct band gap of 2.9 eV. The PECVD pyridine/metacarborane film exhibits indirect and direct band gap energies of 1.4 eV and 3.3 eV, respectively. The data in Fig. 5 and Table. III therefore show that the addition of pyridine or aniline to a PECVD metacarborane film results in smaller direct and indirect band gaps, as is observed for corresponding films incorporating orthocarborane [7,17].

IV. Discussion

The XPS data for PECVD metacarborane, aniline/metacarborane and pyridine/metacarborane films indicate that these materials exhibit many similarities in chemical bonding to corresponding films involving orthocarborane, including N-B bond formation in pyridine-containing films, and an absence of N-B bond formation in aniline-containing films [7,17]. A significant difference, however, is observed regarding aromatic-free PECVD metacarborane films compared to aromatic-free PECVD orthocarborane films. PECVD films derived from orthocarborane, without aromatic doping, exhibit substantial C bonding to B in

extra-icosahedral environments [20], evidently as hydrocarbon bridging groups between orthocarborane icosahedra [34]. Instead, PECVD films derived from metacarborane exhibit no significant evidence of extra-icosahedral C (Fig. 1 h). Whether this difference is due to some slight difference between the PECVD conditions employed here as compared to the previous study [20], or to some more systematic difference in the effects of plasma environments on the two different carborane isomers, cannot be determined from the existing data.

The experimental data indicating a narrowing of band gaps for aromatic/metacarborane composite films relative to the PECVD metacarborane film (Fig. 5) are in good agreement with the calculated densities of states derived from bimolecular cluster calculations (Fig. 3). As shown in Table III, there is close agreement between calculated HOMO-LUMO gaps and experimentally determined direct gaps for the PECVD aniline/metacarborane, PECVD pyridine/metacarborane, and PECVD metacarborane films. The DFT results (Fig. 3) clearly indicate that band gap narrowing in the aromatic/metacarborane films relative to the PECVD metacarborane-derived film is due to the appearance of extra states at the top of the valence band, rather than changes at or near the conduction band minimum. This has also been observed for aromatic-doped orthocarborane-derived films [7,14,33]. The good agreement between experimental and theoretical calculations for PECVD composite films of aromatics and orthocarborane or metacarborane suggests that DFT-based cluster calculations of the type discussed here can have considerable predictive value.

V. Summary and Conclusions

Composite films formed from aniline/metacarborane, pyridine/metacarborane and metacarborane have been fabricated by PECVD and characterized by XPS, VASE and first-principles DFT-based cluster calculations. Core level XPS data show that N-B bond formation is

observed in the pyridine/metacarborane film, but N atoms are not involved in bonding formation in aniline/metacarborane composite film. DFT calculations are consistent with the experimental XPS data, and indicate that N-B bonding configurations are significantly lower in energy than C-B bonding configurations in pyridine/metacarborane bimolecular clusters, but slightly higher in energy in aniline/metacarborane bimolecular clusters. DFT cluster calculations also indicate significant narrowing of HOMO-LUMO gaps in the aniline/metacarborane and pyridine/carborane bimolecular clusters relative to a bi-metacarborane cluster due to the addition of states near the top of the valence band associated with the aromatic moiety. In contrast, states near the conduction band minimum include those associated with either aromatic or metacarborane moieties.

VASE data reveal indirect (direct) band gaps of 1.0 eV (2.9 eV), 1.4 eV (3.3 eV) and 2.6 eV (4.9 eV) for PECVD aniline/metacarborane, PECVD pyridine/metacarborane and PECVD metacarborane-derived films, respectively. In each case, the experimental value of the direct band gap agrees, to within experimental error, with the calculated HOMO-LUMO gap.

In summary, the aromatic/metacarborane films prepared by PECVD co-deposition of metacarborane and aniline or pyridine display many properties in common with orthocarborane analogs, including a narrowing of direct and indirect band gaps upon addition of aromatics, and the absence of N-B bond formation in aniline/carborane composite films [7,16]. One difference appears to be that in PECVD orthocarborane-derived films, XPS reveals substantial C in extra-icosahedral bonding environments as a linkage between icosahedra [20], but this feature is absent in XPS spectra of PECVD metacarborane films. The generally analogous trends in structures and properties of aromatic/carborane films involving metacarborane or orthocarborane, suggest

the possibility of aromatic/carborane p-n junctions formed with composite films involving metacarborane (n-type) or orthocarborane (p-type) [1].

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Tables

Table. I. Total energies and relative stabilities of aniline/metacarborane and pyridine/metacarborane isomorphs in Fig. 2.

Structure	Total energy (eV)	ΔE (eV)
a: B₁₀C₂H_x:AN(B-N)	-16831.937	-
b: B₁₀C₂H_x:AN(B-C)	-16832.209	-0.272
c: B₁₀C₂H_x:PY(B-N)	-15777.948	-
d: B₁₀C₂H_x:PY(B-C)	-15761.825	0.075

Table. II. B-H/B-B ratio based on FTIR (supplemental information, Fig. S1) for PECVD orthocarborane and PECVD metacarborane films.

PECVD film	B-H stretching		B-B stretching		B-H/B-B ratio
	FTIR wavenumber	area under curve	FTIR wavenumber	area under curve	
orthocarborane	2580 cm ⁻¹	13.7	1370 cm ⁻¹	3.0	4.6
metacarborane		1.0		0.2	5.0

Table. III. Summary of Band Gap barrier based on Spectroscopic Ellipsometry and DFT calculations, for PECVD aniline(AN)-metacarborane (*m*-Carborane) films; PECVD pyridine (PY)-*m*-carborane films; and for PECVD *m*-carborane films.

PECVD Films	Ellipsometry		Molecular Orbitals
	Indirect Band Gap	Direct Band Gap	HOMO-LUMO gap
<i>m</i> -Carborane/AN	1.0 ± 0.5 eV	2.9 ± 0.5 eV	2.7 eV
<i>m</i> -Carborane/PY	1.4 ± 0.5 eV	3.3 ± 0.5 eV	3.5 eV
<i>m</i> -Carborane	2.6 ± 0.5 eV	4.9 ± 0.5 eV	4.8 eV

Figures Captions

Figure. 1. Experimental core level photoemission B 1s, C 1s and N 1s spectra for pyridine/metacarborane composite film with ratio of 3:1 are shown a, b and c, respectively. Corresponding data are shown for a composite film aniline/metacarborane ratio of 3:1 in d, e and f. B 1s and C 1s spectra for pure PECVD metacarborane film is shown in g and h.

Figure. 2. Schematics of boron carbide cluster structures showing B-N and B-C bonding formation during PECVD between aniline and metacarborane in Fig. 2 a and b. Corresponding data are shown for pyridine/metacarborane in Fig.2 c and d. The metacarborane-metacarborane structure is shown in Fig. 2 e. Hydrogen atoms on the molecules were for clarity.

Figure. 3. Calculated molecular orbitals band density of states (DOS) of (a) metacarborane-metacarborane cluster, (b) pyridine/metacarborane cluster, (c) aniline/metacarborane cluster. HOMO-LUMO gaps are marked by arrows.

Figure. 4. Plots of experimental psi (Ψ) and delta (Δ) values (solid lines) and fitted Cauchy model values (dotted lines) of PECVD aniline/metacarborane of 3:1 (a, b); pyridine/metacarborane of 3:1 (c, d); PECVD metacarborane (e, f) with angles of incidence from 45° (black), 50° (red), 55° (blue).

Figure. 5. VASE optical absorption data plotted $\alpha^{1/3}$ or α^2 against photon energy for films: a 3:1 aniline/metacarborane ratio derived films (a, b); a 3:1 pyridine/metacarborane film (c, d) and a metacarborane film (e, f). Dashed line were used to present linear relationship of α^N vs E_g .

Figures

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5