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Semi-transparent conductive carbon films synthesized by sintering spin-coated sp^3-based network polymer

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Abstract

We synthesized semi-transparent conducting thin film of amorphous carbon from sp^3-rich network polymer precursor. It showed a reasonable optical transparency (58 - 73% transmission in the wavelength range of 380 - 2200 nm), low electric resistivity (6.7×10^{-3} Ωcm) and durability against corrosive chemical reagents. The sintering involves the formation of graphitic network and the preferential vaporization of sp^2 species.

sp^2-rich amorphous carbon, sometimes called "glassy carbon" when sp^2 content is close to 100%, shows excellent properties such as resistance to corrosive reagents, high electric conductivity, and thermal and mechanical stability[1]. The synthesis of the glassy carbon involves pressure molding of thermosetting resins followed by sintering carbonization at 1300 - 3000 ^{o}C.[2,3] The glassy carbon is used in the form of bulk materials including thick plates, rods, and crucibles for the applications in electrochemical analysis and tools in semiconductor industries. However, thin film forms of the glassy carbon are rarely found in the literature, which may be used for the optically transparent and electrically conductive applications if successfully synthesized. It is reported that some of amorphous carbon (mainly classified as diamond like carbon (DLC)) can become conductive by doping of sp^2 carbon species or other elements, which has been achieved by a variety of synthetic techniques. Those include flash evaporation [4], magnetron sputtering[5], plasma chemical vapor deposition (CVD)[6,7], thermal CVD [8-10], pulsed laser deposition[11], high pressure and high temperature treatment[12-14], casting of finely milled coals[15] and so on. However, optical transparency of amorphous conductive carbon has not been reported to the authors' knowledge.

The present work reports the synthesis of highly conductive (6.7×10^{-3} Ωcm) and semi-transparent (58-73% transmission in visible region) amorphous carbon films with the thickness of ~20 nm with smooth surfaces. The resistivity is much higher than that of DLC and corresponds to that of the glassy carbon. It was synthesized by sintering spin-coated precursory polymer called "poly(hydridocarbyne)", pHC afterwards. It is $(CH)_n$ in an ideal formula, synthesized from the Wurtz reaction between $CHBr_3$ and NaK[16]. We spin-coated its solution onto quartz glass and sintered it at various temperatures. The sintering process was monitored by Raman and optical transmission spectroscopy and electrical measurement. Carrier concentration and mobility were characterized at room temperature and 7 K by Hall measurements.

The synthesis of pHC has been reported by Bianconi[16], Sun[17-19] and Nur and others [20-22]. We have developed an improved method using highly purified reagents, alkali-metal rich condition and sufficient cooling to suppress side reactions, which will be described elsewhere[23].

All the organic reagents were purchased from Kanto Chemical Co., Inc. Tetrahydrofrane (THF) without a stabilizer was purified by distillation after molecular sieves treatment. Bromoform ($CHBr_3$) with ethanol as a stabilizer were extracted from water mixture to remove ethanol and then purified by freeze-pump-thaw cycling and further by using alumina column chromatography. Ar glovebox was used for the

reaction, in which ultrasonic mixer with a teflon beaker was installed. The concentration of the CO_2 in the glove box was monitored and kept always lower than 20 ppm during the synthesis of pHC. In addition, the synthesis was carried out under the NaK-excess condition to avoid α- elimination reaction. Eutectic NaK alloy (3.33mL) dispersed in THF solution (100mL)(NaK-THF solution) was added in the $HCBr_3$-THF solution slowly while being sonicated and the temperature of the solution was kept lower than -5 °C. After the addition of the NaK-THF solution, the sonication was continued for 2.5 hours. After the reaction was completed, ultrapure water (3 mL) was added to the THF solution to quench the residual NaK alloy. The pHC was obtained by extraction using dichloromethane. The typical yield was ~ 10 %.

As-synthesized polymer was characterized by elemental analysis, ^{1}H-NMR, size exclusion chromatography (SEC). Elemental analysis was performed using CHN elemental analyzer CE440 (EAI).

3 mg of the synthesized pHC was dissolved in dichloromethane 100 μL and 20 μL of the solution was dropped quickly while the 1 cm×1 cm quartz glass substrate was rotating at the speed of 5000 rpm on a spin-coater. The rotation was continued for 30 s for the drying. The sample was heated to 600 °C－1000 °C in a tube furnace at the heating rate of 4 °C / min under N_2 gas flow with 100 sccm. The maximum temperatures were kept for 3 hours and the heater was switched off. After cooling the sample, they were characterized by Raman spectroscopy (Renishaw Invia with 532 nm excitation under ×50 objective lens). The optical transmission spectroscopy was taken from 200－2200 nm using Lambda 900 spectrometer. Carrier concentration and mobility were characterized at room temperature and 7 K (a closed cycle refrigerator) by Hall measurements using van der Pauw geometry. X-ray diffraction of the films was measured by Rigaku Miniflex 600.

The results are described in the following. First we examined the synthesis of precursor polymer. The synthesis of the precursor polymer pHC uses Wurtz reaction between $CHBr_3$ and NaK alloy under sonication. There seems to be a problem of reproducibility, *i.e.*, deviation of the results among literatures. Bianconi et al. reported the successful synthesis of pure three-dimensional polymer with sp^3 carbon atoms[16], whereas Sun and others reported that the contamination by sp^2 components and oxygen atoms was unavoidable.[17-22] We modified the procedure from the original papers. In brief, we noticed side reactions were severe problems for the reproducibility. To

suppress the side reactions, we controlled the temperature, suppressed CO_2 concentration below 20 ppm and produced $CHBr_3$ - surplus conditions. As a result, we obtained a powder showing yellow-white color while the others reported brown powders. ^{1}H-NMR spectra of the products before and after the improvement of the synthetic procedure are shown in Fig. 1. It is obvious that concentration of sp^3 component is substantially increased. The molecular weight of the product of modified procedure is ~ 10000 as measured by SEC. The new product was very soluble to $CHCl_3$ (> 50mg / 1mL) and suitable for spin coating. On the other hand, the product from the previous procedure (Fig. 1(a)) does not dissolve well in solvents and it was difficult to obtain uniform films from it.

Next we characterized the formation of carbon films by sintering the pHC from the evolution of Raman spectra. The measurements were done at room temperature after stopping the heating at (a) 600 °C, (b) 800 °C and (c) 1000 °C. The peaks around 1330 cm^{-1} and 1580 cm^{-1} are D-band and G-band, respectively. The D-band corresponds to sp^3 carbons or defects in graphite, while the G-band indicates the existence of extended sp^2 species. Two things are noticed. Signal intensity steeply decreased as the sintering temperature was increased ((b) 1/5 and (c) 1/30 compared with (a)). G-band decreased more than D-band as the sintering temperature increased. The former means that the part of the film was vaporized during the sintering, and the latter means that sp^2 component is lost more quickly. The Raman spectrum of the final product (Fig. 2(c)) resembles that of the DLC. This result, faster evaporation of sp^2 carbon species, explains why sp^3- rich DLC (or, reportedly, microcrystalline diamond or lonsdalite as a minor component in some cases[16) 25)]) remains as a final product even from the sp^2 containing impure pHC or other poly(phenylcarbine)[24)] or poly(arkylcarbine)[25)].

Next we measured the optical transmission spectra of the thin films after heating to the temperatures from 600 °C to 1000 °C (Figs. 3 (b)-(f)). Precursor pHC film before the sintering is also shown in Fig. 3(a). Figure 3(a) shows almost complete transmission from 480 nm to 2200 nm, which corresponds to mainly sp^3 nature of the precursor film with sp^2 impurity without extended conjugation. After heating at 600 °C (Fig. 3(b)), the film showed a broad absorption in the visible region. Then the spectrum become rather flat at 700 °C (Fig. 3(c)) but the absorption was strong (~50% transmission at 1000 nm). The change of the film composition will be discussed later. The absorption decreased when the sintering temperature increased, and at 1000 °C the transmission recovered to 73 % at 780 nm. It shows minimum transmission in the visible region 58 %

at 380 nm.

X-ray diffraction of the films (not shown) did not show distinct peaks but only a very broad feature even with multiple coating and sintering at various temperatures, which indicates the amorphous nature of the films. The thickness of spin-coated thin films of pHC was evaluated from the laser optical microscopy with a piezoelectric stage. The height can be evaluated by optical focusing as shown in Figs. 4(a) and (b). A part of the film was wiped out with acetone to evaluate the film thickness using the boundary. Although the signal contains noise, the average thickness can be estimated as 100 nm. Figures 4(c) and (d) show an AFM image and its cross sectional plot, respectively, of the film boundary after sintering at 1000 °C. The boundary created by wiping the precursor makes protrusion, but we can see the thickness is approximately 21 nm. The AFM images of the quartz glass substrate and the film after sintering at 1000 °C are shown in Figs. 4(e) and (f), respectively. The RMS roughness of the film is approximately 2 nm.

Electric properties of the films are summarized in Table 1. The films sintered at 600 °C and 700 °C did not show sheet resistance below 20 MΩ square, but the films started to become conducting after heating at the temperatures higher than 800 °C. The Hall measurement of the film sintered at 1000 °C showed the electric resistivity of 6.7×10^{-3} Ωcm. It showed degenerate semiconducting or dirty metallic behavior in which the carrier concentration did not change significantly at low temperature. As long as the resistivity is involved, the film sintered at 1000 °C is close to glassy carbon.

Chemical stability of the films was evaluated by RCA treatment that is used in semiconductor industry (80 °C H_2O_2+HCl and H_2O_2+NH_3)[26] and by immersing the films in concentrated H_2SO_4 for 24h at RT. The appearance of the films and the resistivity were not changed by these treatments.

We obtained a new thin film material that shows reasonable optical transparency, low electric resistivity and chemical stability in corrosive environment. We will discuss the nature of this material and the reactions occurring during the sintering of the films. Figure 5 illustrates the change in the chemical structure of the films during the sintering. The precursor pHC was a polymer mainly consists of sp^3 carbon and hydrogen (Fig. 5(a)). The optical transparency was high and does not show electric conductivity. When it was heated to 600 °C, it contain π-conjugated sp^2 carbon with a certain length (*e.g.* 3-10 atoms, Fig. 5(b))[27-28] because it shows the wide optical absorption in the visible region (Fig. 3(b)). However, the π-conjugated species were not

connected because the film did not show electric conductivity. When the sintering temperature was increased, the π-conjugated carbon atoms became connected with each other to make graphitic species, and the electric conductivity appears (Fig. 5(c)).

The overall thickness of the film decreases from 100 nm to 21 nm by vaporization of hydrocarbon species.[29] It seems that the evaporation of sp^2 species preferably occurs, because the G-band of Raman decreases more rapidly. We believe that the vaporization is not due to oxidization by contamination of environmental gas flow (N_2), because prolonged heating did not cause the reduction of the film thickness. The electric conductivity must come from extended sp^2 network like graphite or glassy carbon. It should be noted that the resistivity (6.7×10^{-3} Ωcm) is lower than conductive amorphous carbons except for glassy carbons in the literature. From the comparison with previous reports, the nature of the precursor polymer pHC, which contains sp^3 network with small number of hydrogen, is important to produce very thin amorphous carbon coating with reasonable transparency and conductivity. We consider that the lack of grain boundary in the film is important for the low resistivity observed here.

It is probably difficult to apply this film as a transparent conductor because of the high process temperature and properties inferior to other candidates such as metal oxides,[30,31] graphene,[32] and metal nanowires[33]. Nevertheless it will find a certain application in electrochemistry [34], semiconductor industry, or solar energy conversion [35] because of the chemical stability and surface smoothness.

To summarize, we synthesized very thin film (~20 nm) of amorphous carbon from sp^3-rich network polymer precursor. It showed a reasonable optical transparency (58-73% transmission in the wavelength range of 380 - 2200 nm), low electric resistivity (6.7×10^{-3} Ωcm) and chemical durability. The sintering process was studied by Raman and optical transmission spectroscopy. The film sintering involves with the formation of graphitic network and the preferential vaporization of sp^2 species.

Table1：Electrical properties of a film sintered at 1000 °C.

measured temperature	at 7 K	at 298 K
resitivity / Ωcm	1.3×10^{-2}	6.7×10^{-3}
carrier conc. / cm^{-3}	4.9×10^{20}	1.4×10^{21}
mobility /$cm^2V^{-1}s^{-1}$	0.94	1.5

Figure captions

Fig. 1: 1H-NMR of poly(hydridocarbine) synthesized after (a) the procedure in literatures and (b) modified procedure.

Fig. 2: Raman spectra of the carbon films after sintering at (a) 600 °C, (b) 800 °C, and (c) 1000 °C.

Fig. 3: Optical transmission spectra. (a) Precursor polymer film. (b) - (f) After sintering at (b) 600 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C and (f) 1000 °C.

Fig. 4: Morphology of the films. (a) Laser microscope image of the precursor polymer (pHC) film near the boundary. (b) Cross section derived from focusing of (a). (c) AFM image of the conducting carbon film obtained by sintering at 1000 °C. (d) Cross section derived from focusing of (c). (e) AFM of quartz glass substrate (root-mean-square roughness 0.68 nm) (f) AFM of carbon film after sintering at 1000 °C (root-mean-square roughness 2.0 nm)

Fig. 5: Model structures during carbon film formation by sintering. (a) Precursor polymer, (b) visible light absorbing film at intermediate temperature (*e.g.* 600 °C), and (c) highly conducting semi-transparent film obtained by sintering at 1000 °C.

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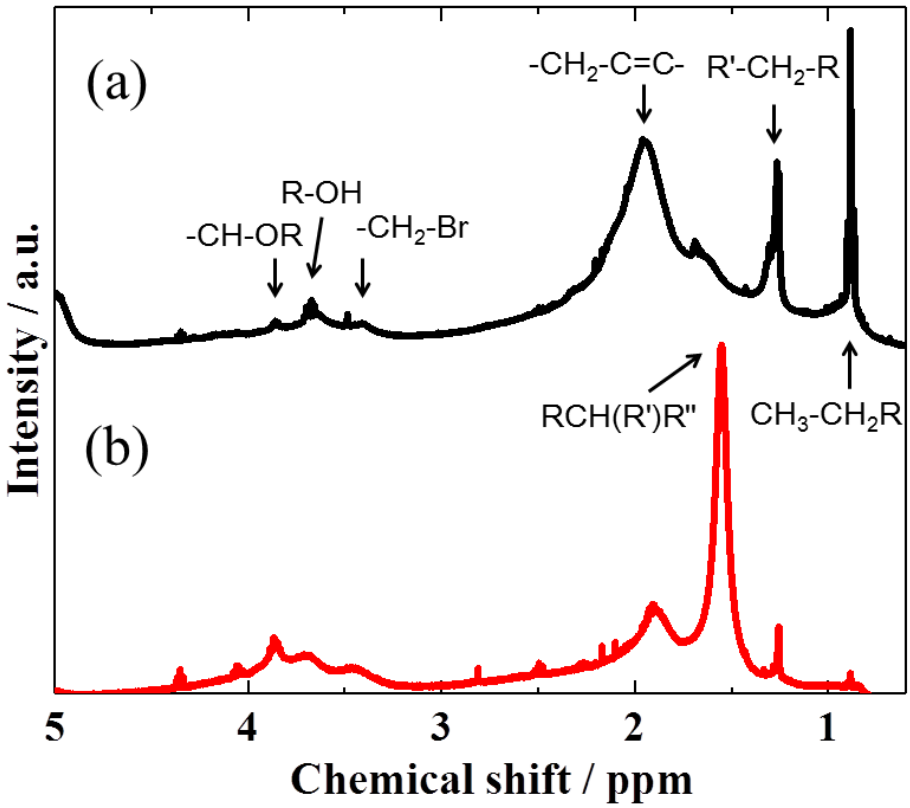

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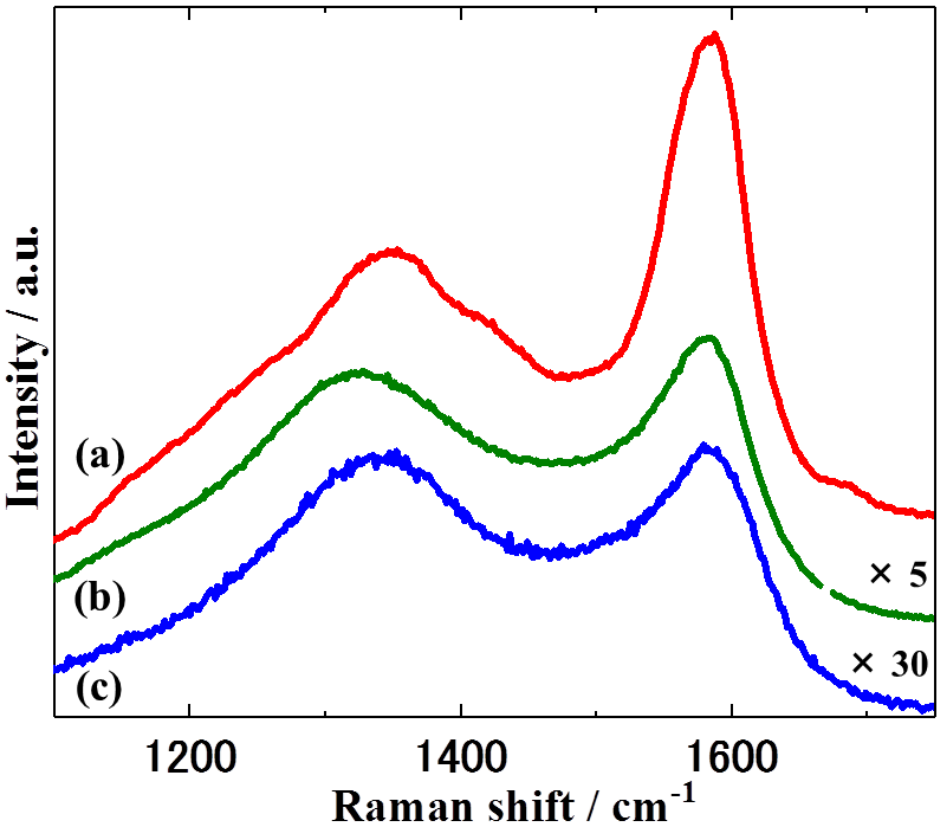

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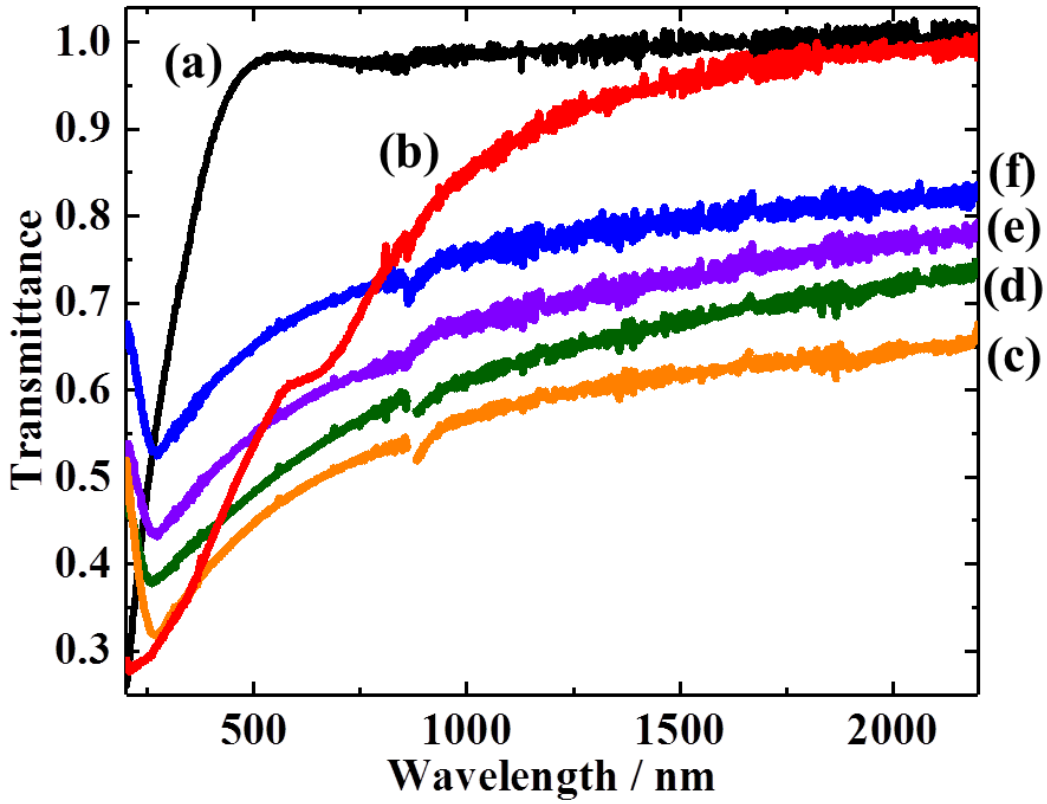

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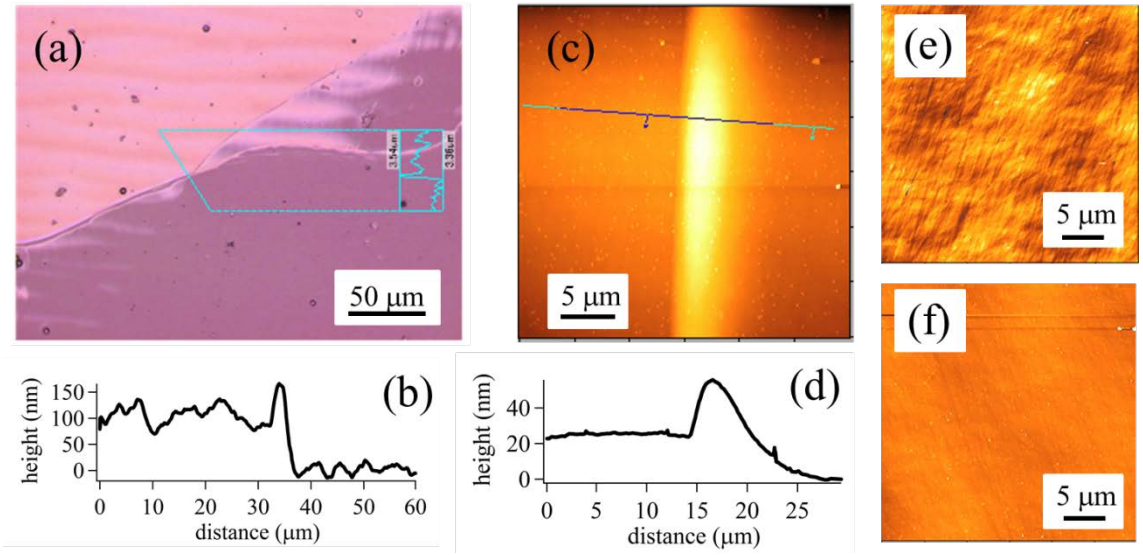

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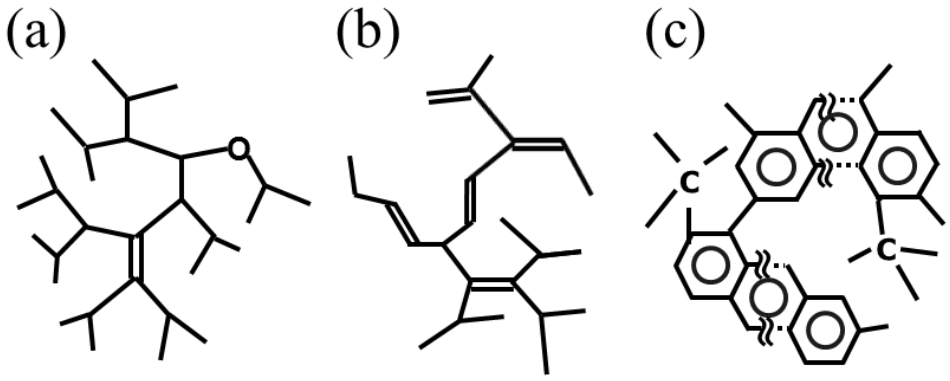

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