# Laser-Assisted Deposition of Pure Gold from (CH<sub>3</sub>)<sub>2</sub>Au(hexafluoroacetylacetonate) and Gas-Phase Luminescence Identification of Photofragments

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Pure gold films are deposited on germanium, silicon, silicon dioxide, and quartz by photolyzing  $(CH_3)_2Au$ -(hexafluoroacetylacetonate) in the gas phase. Shiny gold films are deposited at low incident fluences (<5 mJ/cm<sup>2</sup>), whereas higher fluences yield dull brown deposits. The effects of the fluence and the repetition rate of the pulsed laser on the morphology of the deposited film are studied by using SEM. The film quality is analyzed by using XPS and Auger spectroscopic methods. No detectable carbon is found in either the gold or brown films, indicating that both are pure gold with different surface morphologies. Luminescence in the gas phase is observed under the conditions used for the photodeposition. The emission spectrum, containing two bands having well-resolved vibronic fine structure, originates from dimeric gold, Au<sub>2</sub>. The spectroscopic identification of ligand-free gold indicates that there is a gas-phase photochemical component in the deposition process. Deposition mechanisms, including both a surface component and a gas-phase component, are discussed.

# Introduction

Gold is an extremely important metal in microelectronic applications. The high conductivity and relative inertness promote its use for interconnects. Interconnects require a patterning method for use. The most common method involves evaporation of gold and photolithography to achieve the necessary patterns. This method exposes the surface to numerous organic solvents and requires a number of steps.

To reduce the number of steps and to obviate the need for laying organic polymers on the semiconductor surface, a number of methods have been used to directly write the necessary patterns. Focused ion beams have been used to provide the energy necessary to deposit gold from the volatile gold precursor.<sup>1</sup> Another method is to use light to provide the energy for decomposition and to spatially delineate the deposition region.

Light-induced deposition of films can be divided into two categories of mechanisms: photothermal and photolytic. In a photothermal mechanism, the light is of a frequency that is not absorbed by the volatile metal precursor but is absorbed by the substrate. The absorption of energy leads to heating of the substrate which, if above the decomposition temperature of the gaseous precursor, leads to film growth. In this photothermal mechanism, the growth rate is not dependent on the wavelength of the light unless there is a wavelength dependence for the substrate absorption. The heating of the substrate surface can lead to alteration of the substrate. Comita and co-workers observed melting of the gold films during growth.<sup>2</sup> In spite of potential problems, many good results have been achieved using a photothermal technique.<sup>3,6</sup>

The second, less common mechanism for film growth is direct photolytic decomposition of an organometallic precursor. This mechanism requires the use of a wavelength of light which matches an absorption band of the precursor that leads to fragmentation. The substituents on the metal must all be lost to achieve a pure film. Baum and co-workers deposited films photolytically from  $Me_2Auacac$  (dimethyl gold acetylacetonate) with very poor results and concluded that photolytic deposition would inherently give impure films.<sup>7-9</sup> The films contained a high quantity of carbon, sometimes in excess of 50%. We explored the possibility that the high carbon incorporation was due to the choice of ligands, by studying the extent of carbon incorporation in films made by photolytic decomposition of the organometallic compounds Me<sub>2</sub>-Auhfacac (dimethyl gold hexafluoroacetylacetonate), Me<sub>2</sub>-Autfacac (dimethl gold trifluoroacetylacetonate), and Me<sub>2</sub>-Auacac. The carbon incorporation was found to inversely follow the level of fluorination, with no detectable carbon being observed with the use of Me<sub>2</sub>Auhfacac.<sup>10a</sup> It is therefore important to understand the mechanisms by which the decomposition is occurring to possibly extend the process to other compounds.

During the course of the deposition studies, a dim luminescence was observed in the path of the laser beam in the deposition cell. In response to this discovery, a spectroscopic study was conducted to determine the origin of the luminescence. The emission spectra showed that the luminescence did not originate from the Me<sub>2</sub>-Auhfacac starting material that was loaded into the cell, but rather from gas-phase photofragments produced under the same experimental conditions as the final photodeposit. Vibronic fine structure was observed on the luminescence bands. These observations opened the possibility of using spectroscopy to identify the photointermediates that were produced during the deposition process and thus provide insight into the deposition mechanism.

In this paper we report the laser-assisted metalorganic chemical vapor deposition (MOCVD) of pure gold by irradiating Me<sub>2</sub>-Auhfacac in the gas phase. The effects of the fluence and the repetition rate of the pulsed laser on the morphology of the deposited film are described. The film purity is analyzed by using XPS and Auger methods. The emission spectra of the gas-phase photofragments observed under the deposition conditions are reported. The vibronic structure on the emission bands is used to identify one photofragment. The possible role of the photofragment in the deposition mechanism is discussed.<sup>10b</sup>

# **Experimental Section**

**Compounds.** Dimethyl gold hexafluoroacetylacetonate was prepared by placing 2 g of AuBr<sub>3</sub> under argon in 30 mL of sodiumdried ether. The solution was cooled in a dry ice-acetone bath; 38 mL of 0.36 M MeLi in ether was added dropwise over 45 min

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Figure 1. Experimental setup for the photolytic deposition of gold films.

with stirring, and 0.64 mL of hexafluoroacetylacetone in 30 mL of dry ether was then added dropwise over 45 min. The solution was allowed to warm and 75 mL of water added. The aqueous fraction was separated and extracted twice with ether. The combined organic layers were washed twice with water and dried with anhydrous magnesium sulfate, filtered, and vacuum distilled to yield 100 mg of a yellow liquid. The IR spectrum matched that reported in the literature.<sup>11</sup> The overall yield of 8% (with no attempt to optimize the synthesis) was comparable to that of the multistep optimized literature synthesis via the  $[Me_2AuI]_2$  intermediate.<sup>12-14</sup>

The deuterated complex was formed by reaction of 2 equiv of methyl- $d_3$  lithium with gold tribromide to yield  $[(CD_3)_2AuBr]_2$ . The complex was purified as described in the literature<sup>14,15</sup> by reaction with ethylenediamine and regeneration with HCl. Deuterodimethyl gold hexafluoroacetylacetonate was obtained by reacting  $[(CD_3)_2AuBr]_2$  with 2 equiv of thallium hexafluoroacetylacetonate in ether. The thallium bromide precipitate was removed by filtration. The yellow product was obtained by vacuum distillation.

Film Growth. Gold films were grown using an XeCl excimer laser operating at 308 nm. The laser beam was expanded and an aperature used to obtain a uniform fluence region from the beam. Deposition areas were typically a square centimeter. The apparatus in Figure 1 was used to deliver the source material to the sample region. This apparatus directs the gas at the substrate so that the largest concentration of metal precursor will be near the substrate surface. A window purge with helium is used to eliminate deposition on the quartz entrance window. A throttling valve maintains the pressure at a preselected level and mass flow controllers deliver a precise quantity of carrier diluent gas and deposition precursor compound.

Film Characterization. The XPS experiments were conducted on a VG Mark II ESCA lab instrument using an Al K $\alpha$  (1486.6 eV) X-ray source. The fwhm of Au  $4f_{7/2}$  of a clean Au foil was 1.61 eV and the sensitivity to carbon was approximately 1%. To investigate the purity of some of the films, approximately 100 Å were removed by sputtering with xenon prior to analysis. Film thickness was measured by shadowing a portion of the wafer and using a Dektak instrument to measure the step height.

Spectra. The gas-phase luminescence spectra were obtained by exciting the sample in a two-window cell with 308-nm radiation from a XeCl excimer laser. The laser beam (25 mJ/pulse, 20 Hz repetition rate) was focused into the cell by using a 10 cm focal length  $CaF_2$  lens. The emitted light was collected at right angles to the excitation beam, passed through a 0.3-m JY monochromator with a 600 grooves/mm grating, and detected with an EG&G OMA3 diode array detector. The cell was constructed so that the sample chamber is separate from the luminescence part of the cell. To fill the cell with precursor gas, the luminescence part of the cell was evacuated to roughly 200 mTorr, the cell was closed, and then the precursor was allowed to establish its equilibrium vapor pressure. Once the precursor was added, the pressure conditions under which the spectra were



Figure 2. XPS spectrum of the pure gold film.

taken could be varied by the addition of argon, as a buffer gas, through a different entrance port.

The gas-phase ultraviolet-visible absorption spectra were taken in a specially constructed UV cell attached to a Vacuum General capacitance manometer gauge for pressure determination. A Perkin Elmer Lambda 9 spectrometer was used to acquire the spectra.

The solid-state emission spectrum of the frozen starting material was measured using an Air Products displex closed-cycle refrigeration system for cooling. Two different excitation wavelengths were used, the 351-nm radiation from an  $Ar^+$  laser and the 308-nm radiation from an excimer laser. The spectra measured for the different excitation energies are identical. The emitted light was collected and passed through a 0.75-m Spex monochromator and then detected by a C31034 photomultiplier tube.

#### Results

Laser-Assisted MOCVD of Gold Films. Shiny gold films were deposited at low incident fluences ( $<5 \text{ mJ/cm}^2$ ) on germanium, silicon, silicon dioxide, and quartz. The appearance of the films was shiny for all cases where the fluence was low. Higher fluences yielded dull brown nonshiny deposits.

The pulse repetition rate was found to influence the deposition rate but not the quality of the films up to the highest rates in these experiments (40 Hz). This result indicates that the time between pulses was sufficiently long to bring in new material and to sweep away any intermediates and leave no pulse to pulse memory. Depositions carried out at higher repetition rates may eventually become source limited, or intermediates may accumulate and change the growth rate and quality of the film.

The quality of the films was examined by using both Auger spectroscopy and XPS. In both cases the surfaces contained large quantities of carbon, which came either from the air transfer to the analytical instrument or from remnants of the deposition. Sputtering of the films and depth profiling revealed no detectable carbon in the interior of the gold films (<1% resolution), as shown in the XPS spectrum in Figure 2. The brown, nonshiny films gave an analysis identical to that of the shiny films indicating that both types of film are pure gold but that the surface morphologies are different.

The morphology of the brown films and the shiny gold films were studied by using a SEM. A picture of the surface of the brown film is shown in Figure 3. The surface has the appearance of small spheres packed together. The spheres have a diameter of approximately 0.1  $\mu$ m with clumps occurring which are larger than 0.5  $\mu$ m. This morphology explains the lack of shininess of the films; the clumps scatter the incident radiation and give a dull appearance. The shiny gold films were smooth to the limit of Laser-Assisted Deposition of Pure Gold



Figure 3. Scanning electron microscope (SEM) picture of the surface of the brown gold films deposited.

resolution of the SEM (<0.1  $\mu$ m) with an occasional sphere lying on the surface.

**Luminescence Spectra.** The gas-phase luminescence was observed during the deposition studies under low fluences ( $<5 \text{ mJ/cm}^2$ ). The gas-phase emission spectrum measured under these conditions is the same as that in Figure 4, except that the signal to noise ratio was much lower. In order to increase the signal to noise ratio, the fluence was increased ( $>10^3 \text{ mJ/cm}^2$ ) during the spectroscopic measurements.

The gas-phase emission spectrum resulting from 308-nm excitation of the deuterated Me<sub>2</sub>Auhfacac contains two main bands containing vibronic structure, one centered at about 25 000 cm<sup>-1</sup> and the other at about 19 000 cm<sup>-1</sup>. The spectrum of the band in the region of 19 000 cm<sup>-1</sup> is shown in Figure 4. The vibronic structure in the spectrum of the protonated molecule is identical to that in the spectrum of the deuterated molecule.

The emission spectra of the protonated and deuterated Me<sub>2</sub>-Auhfacac complexes were taken at low temperature in the condensed phase so that the luminescence spectra of both of the parent compounds could be compared to the gas-phase luminescence spectra. The emission spectra of the frozen liquid Me<sub>2</sub>-Auhfacac at 15 K is shown in Figure 5. The condensed-phase emission spectrum consists of one band containing vibronic structure with the peak maximum centered at about 20 000 cm<sup>-1</sup>. The spacing between the largest peaks is about 1352 cm<sup>-1</sup>, much larger than any spacing observed in the gas-phase spectra. Therefore, the luminescence of the frozen compound and that obtained in the gas phase originate from different molecules.

Absorption Spectra. The electronic absorption spectra of  $Me_2$ -Auhfacac in both the gas phase and liquid phase (neat) were taken in the 200–500-nm wavelength region. The gas-phase spectrum contains a band centered at 320 nm containing poorly resolved vibronic structure. The absorbance at 351 nm, the wavelength of the  $Ar^+$  laser used in the photolysis, is roughly half that of the band maximum. The onset of a more intense shorter wavelength absorbance is observed at about 250 nm. The solution



Figure 4. Gas-phase emission spectrum of  $Au_2$  resulting from photofragmentation of deuterated Me<sub>2</sub>Auhfacac.



Figure 5. Solid-phase emission spectrum of Me<sub>2</sub>Auhfacac measured at 15 K.

absorption spectrum at higher concentrations was obtained in order to search for weaker bands at longer wavelengths. An absorption was found centered at about 420 nm with an extinction coefficient of about  $0.7 \text{ M}^{-1} \text{ cm}^{-1}$ . The band has resolved vibronic structure with peaks at 435, 415, and 390 nm. The relative intensities of the vibronic bands roughly mirror those observed in the emission spectrum shown in Figure 5. The onset of this absorption band overlapped the emission band of the frozen liquid in the 450-nm region.



Binding Energy (eV)

Figure 6. XPS spectrum of the gold spectral region (thick line), the Gaussian fit of two doublets and the overall fit (dotted lines) for Me<sub>2</sub>-Auhfacac adsorbed to a germanium surface and exposed to one 308-nm laser pulse. The full width half-maximum of the gaussians are 1.2, 1.8, 1.3, and 1.5 eV for the 83.6, 84.8, 87.2, and 88.3 eV peaks, respectively. The percent areas are 35.7, 20.7, 26.5, and 17.1, respectively.

#### Discussion

1. Deposition. A possible explanation for the change in morphology with increased fluence is a change from surface film nucleation and growth to a larger component of vapor-phase growth and subsequent deposition. The spheres most likely nucleate in the gas phase and grow radially until they impinge on the surface. The specular films formed at low fluence grow at a rate of approximately 1 monolayer per pulse, implying surface involvement in the film growth.

The involvement of a chemisorbed, possibly dissociatively adsorbed, gold species on the substrate was investigated by using XPS. A germanium substrate was cleaned with water, acetone, and methanol and broken into separate pieces. One sample was used to take a reference XPS of the Ge substrate. A second sample was exposed to the vapor of the gold complex but no laser light. A third sample was exposed to the gold vapor and one pulse of the laser (Figure 6). Finally, a fourth sample had a thick gold deposit grown with ~5000 laser pulses (Figure 2).

The clean reference sample showed no signal from gold while a sample exposed to the Me<sub>2</sub>Auhfacac vapor showed the Au 4f doublet of an adsorbed gold species (84.5, 88.2). The gold signal showed no evidence for loss after 24 h at pressurs less than 10-9 Torr indicating strong chemisorption through either an associative or dissociative mechanism. The latter mechanism would be most consistent with a previous observation of free radicals on the surface.<sup>16</sup> The gold is in an oxidized state as evidenced by the shift in energy from that expected for pure gold peaks ( $\Delta E = 1.13$ eV).<sup>17</sup> The XPS of the sample, which was prepared with one ultraviolet laser pulse to dissociate the gold precursor, revealed the two asymmetric peaks shown in Figure 6. Standard fitting procedures, which use a single doublet, do not allow for an exact fit of the peak areas while maintaining a reasonable fwhm and a 4:3 area ratio required for a 4f doublet. A fit in which two doublets were used with no constraints gave the four-peak decomposition shown by the dotted lines in Figure 6; (83.6, 87.2 eV) 1.35 area ratio, (84.8, 88.3 eV) 1.21 area ratio. The splitting of each doublet, corresponding to the spacing between the  $4f_{5/2}$ and  $4f_{7/2}$  levels, agrees with the literature value of 3.65 eV.<sup>17</sup> This set of doublets fits the spectrum well and the ratios of the doublets are close to 4:3 required. The binding energies are consistent with gold metal (83.8, 87.45 eV) and the initially adsorbed species observed (84.5, 88.2 eV) with no photolysis. Since we obtained a good fit to the spectrum and the fit is internally consistent, other fits using additional doublets to represent the other species were not necessary. These doublets indicate two gold species are

 TABLE I:
 Positions and Assignments of the Most Intense

 Peaks in the Emission Spectrum of Au<sub>2</sub> Excited by Irradiating

 Me<sub>2</sub>Auhfacac in the Gas Phase

obsd peaks (cm <sup>-1</sup> )	Au <sub>2</sub> peaks $(cm^{-1})^a$	assignment (v',v'')
19 633 🛳 5	19 644	0,0
19444	1 <b>9454</b>	0,1
19258	19264	0.2
1 <b>907</b> 1	19076	0,3
18884	18888	0,4
18700	18701	0.5
19774	19786	1,0
19912	19926	2,0
20052	20065	3,0
20184	20205	4.0

<sup>a</sup> Reference 20.

present on the surface upon irradiation: elemental gold and an oxidized adsorbed species. The fourth sample verified that the doublet at 83.6 and 87.2 eV is due to elemental gold as these intense absorptions were the only gold 4f peaks observed.

To verify that the choice of ligands on the gold plays an important role in determining the purity of the resulting films, gold films using dimethyl gold acetylacetonate and dimethyl gold trifluoroacetylacetonate were grown. The diluent gas and the pressure were adjusted to yield a gas-phase concentration similar to that of dimethyl gold hexafluoroacetylacetonate used to grow the pure films. The films grown with the non-fluorinated gold complex gave high carbon impurity levels (79%) as reported by Baum.<sup>9</sup> The trifluoromethyl complex gave a much lower carbon impurity level (29%) as measured by XPS. The data are consistent with the ligand playing a major role in the incorporation of carbon impurities.

Adhesion of the pure gold films depends on the substrate. On silica and halide glasses adhesion is poor. Deposition on germanium conversely yielded a highly adhesive film that survived the tape test.

2. Identification of the Luminescent Photofragment. The luminescence spectrum of  $Me_2Auhfacac$  at 15 K is shown in Figure 5. This emission spectrum overlaps the lowest energy absorption band of  $Me_2Auhfacac$ . The readily apparent vibronic spacing with an energy separation of 1352 cm<sup>-1</sup> corresponds to a ring deformation mode of the molecule and the 262 cm<sup>-1</sup> corresponds to a ring C-C stretching mode in the molecule.<sup>18-20</sup> These modes are observed in the Raman spectrum of the parent compound. For these reasons, the 21 000-cm<sup>-1</sup> emission band is assigned to the intact parent compound and not a photofragment.

The luminescence spectrum observed from excitaion of Me<sub>2</sub>-Auhfacac in the gas phase, in contrast, does not originate from the intact parent compound. The spectrum, shown in Figure 4, contains bands at energies different from that of the parent compound. In addition, the vibronic structure is also very different. The spectrum matches that reported for Au<sub>2</sub> within experimental error.<sup>21,22</sup> The band at 19 000 cm<sup>-1</sup> is the A to X transition in Au<sub>2</sub> and the band at 25 000 cm<sup>-1</sup> is the B to X transition in Au<sub>2</sub>.<sup>21,22</sup> The band at 19 000 cm<sup>-1</sup> consists of several progressions, each with a spacing of roughly 190 cm<sup>-1</sup>, the vibrational frequency of the ground state. The different progressions result from emission from different vibrational levels of the excited state. The peak positions are compared to literature values in Table I.

To further verify that the gas-phase emission spectrum does not originate from the parent molecule, the deuterated methyl complex and the protonated acetylacetonate complex were prepared. The positions of the vibronic peaks in the well-resolved 19 000-cm<sup>-1</sup> band in gas-phase luminescence of the deuterated compound Me<sub>2</sub>Auhfacac were the same within experimental error as those in the protonated compound. If the vibronic structure involved the deuteromethyl groups, there would be a decrease in the vibrational spacing of about 5–10% in the metal-carbon

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stretch. In addition, the vibronic structures in the 19 000-cm<sup>-1</sup> band in the gas-phase emission spectra of Me<sub>2</sub>Autfacac and Me<sub>2</sub>-Auacac are the same within experimental error as that in the Me<sub>2</sub>Auhfacac gas-phase emission spectrum. Changes in the amount of fluorination of the acetylacetonate ligand will affect the energy of most of the normal modes associated with the ligand by changes in mass with electron-withdrawing ability.<sup>23</sup> Because no changes in energy were observed, the luminescent photofragment does not contain the acetylacetonate ligand.

Similar conclusions can be drawn from examination of the vibronic structure in the 25 000-cm<sup>-1</sup> emission band in the gasphase spectra. The structure in this band is not as highly resolved as that in the 19 000-cm<sup>-1</sup> band discussed above. However, within the experimental uncertainty of the measurements, no changes in the spacing of the vibronic bands are observed when CH<sub>3</sub> is replaced by CD<sub>3</sub> or when hfacac is replaced by tfacac and acac. These results, together with the excellent agreement between the measured vibronic energies and those reported in the literature, confirm that the gas-phase emission bands originate from Au<sub>2</sub> and not from the organometallic precursor.

3. Mechanisms of the Laser-Assisted MOCVD. Identification of  $Au_2$  as the luminescent photofragment indicates that there is a gas-phase photochemical component to the deposition mechanism. One possible mechanism for deposition would be that these Au dimers, created in the gas phase, continue to grow into small particles that fall to the surface and form the gold film on the substrate. Photolysis of other volatile organometallic compounds has been shown previously to create metal clusters.<sup>24</sup>

The observed results are consistent with a deposition mechanism involving both surface reactions and gas-phase reactions. The XPS data shows that a chemisorbed gold species is present, consistent with the results of Dubner and Wagner,<sup>25</sup> who followed the adsorption of dimethyl Auhfacac with a quartz crystal balance as a function of temperature and pressure. They noted an irreversible adsorption of approximately 1 monolayer, followed by reversible adsorption layers. The irreversible adsorption was even observed at extremely low pressures (5 × 10<sup>-6</sup> Torr). The nature of the adsorbed species was not discussed.

Dimethyl gold hexafluoroacetylacetonate, like most tetracoordinate gold complexes, is a square planar complex.<sup>26</sup> The chemisorption may occur by overlap of the empty gold  $d_{z^2}$  orbital with a dangling bond on the substrate surface. In this configuration, all of the gold complex molecules would be lying flat, parallel to the surface. The gold oxidation state would be slightly less than that of the free molecule due to electron donation from the surface.

Another possibility for the surface reaction is a dissociative chemisorption. The surface may promote replacement of the methyl groups with surface bonding. In this case, the complex would be oriented perpendicular to the surface to maintain the square planar coordination. Further experiments are necessary to distinguish these possibilities.

The thermal decomposition of dimethyl Auhfacac has been studied. Solution studies<sup>27</sup> and laser thermal modulation surface<sup>28,29</sup> monitored by mass spectrometry showed that there are at least two decomposition mechanisms. The molecule could be decomposing by reductive elimination of ethane followed by decomposition of the unstable Au(I)hfacac molecule. Secondly, the precursor could be decomposed by a radical pathway. The large number of fragmentation products suggests that radicals are being produced. Presumably the methyl groups are sequentially lost followed again by the loss of the hfacac ligand.

The photolytic decomposition does not necessarily follow the same mechanism as thermal decomposition. Photochemical decomposition of Me<sub>2</sub>Auacac in solution was shown to have a greater component of radical decomposition than the thermal process.<sup>15</sup> In the vapor phase, solvation is much less important and reductive elimination of ethane is probably a more significant component. Ethane is less likely to be incorporated in the growing film or gold particulates than radicals. If decomposition through methyl radical intermediates were the dominant pathway, then the methyl radicals would be incorporated in the film independent of the nature of the acac ligand, contrary to observation. Note, however, that as the electron-withdrawing ability of the ligand changes, the ligand's ability to react with methyl radicals may change. The gettering mechanism could also play a role. Further work is necessary to quantify the relative contributions of the different mechanisms.

# Summary

Irradiation of Me<sub>2</sub>Auhfacac in the gas phase with 308-nm laser pulses produces gaseous Au<sub>2</sub> and deposits pure gold films. The film morphology is related to the fluence. At low fluence ( $<5 \text{ mJ/cm}^2$ ), surface film nucleation and growth appear to dominate and specular films are produced. At higher fluences, vapor-phase nucleation and growth become more important resulting in the production of films whose surface has the appearance of ~0.1-µm spheres.

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