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Improvements of Interfacial and Electrical Properties for Ge MOS Capacitor with LaTaON Gate Dielectric by Optimizing Ta Content *

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The interfacial and electrical properties of high-k LaTaON gate dielectric Ge metal-oxide-semiconductor (MOS) capacitors with different tantalum (Ta) contents are investigated. Experimental results show that the Ge MOS capacitors with a Ta content of ∼30% exhibit the best interfacial and electrical properties, including low interface-state density ($7.6 \times 10^{11}\ cm^{-2}\ eV^{-1}$), small gate-leakage current ($8.32 \times 10^{-5}\ A/cm^2$) and large equivalent permittivity (22.46). The x-ray photoelectron spectroscopy results confirm that the least GeO_x is formed at the Ge surface for the sample with a Ta content of ∼30% due to the effective blocking role of Ta against O diffusion and the greatly improved hygroscopicity of LaON.

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High-mobility germanium (Ge) metal-oxide-semiconductor field-effect transistors (MOSFETs) with high permittivity (high-k) gate dielectrics have been extensively investigated to further improve the scaled CMOS technology.[1] However, several hurdles have to be overcome before implementing Ge into a fully CMOS-compatible processing scheme, such as the passivation of Ge surface and a high-quality gate dielectric.[2] Due to its high-k value (25), broad band gap (5.5 eV) and good thermal stability, La-based oxides are widely investigated to be used as both high-k gate dielectric and passivation interlayer,[3–6] and a good interface quality has been demonstrated in the volume of experiments. Moreover, nitrogen (N) incorporation into La_2O_3 could further suppress Ge and O diffusion and improve the interfacial property.[4,7] However, because of its hygroscopic nature, La-based oxides seem unsuitable for being directly used as gate dielectric or passivation interlayer.[8] For solving the problem, Ji *et al.*[9] prepared a LaTaON dielectric used as a passivation interlayer by doping Ta into La-based oxides in N_2 atmosphere, achieving a good interfacial quality and electrical characteristics. Further, Cheng *et al.*[10] reported that incorporation of Ta into LaON can improve its hygroscopic nature, and directly used LaTaON as the high-k gate dielectric of Ge MOS and obtained good results.[11] As a deep study, in this work, the effects of the Ta content in the LaTaON gate dielectric on interfacial and electrical properties of Ge MOS capacitors are further investigated to achieve more excellent high-k LaTaON gate dielectric by optimizing the Ta content.

Ge MOS capacitors were fabricated on n-type (100) Ge substrates with a resistivity of 0.02–0.1 Ω·cm. Prior to the dielectric stack formation, the Ge surface was cleaned in trichloroethylene, acetone, and ethanol in sequence, and finally rinsed in de-ionized water followed by 30-s diluted HF (1:50) dipping for several cycles to remove the native oxide. After drying by N_2 gas, the wafers were immediately transferred to a sputtering chamber. A 10-nm-thick LaTaON film was deposited by co-sputtering La_2O_3 (RF) and Ta (DC) targets at room temperature in an Ar/N_2(=24/6) ambient. The content of Ta was controlled by changing the sputtering power of the Ta target. Then, a post-deposition annealing (PDA) was carried out in N_2 (500 sccm)+O_2 (50 sccm) ambient at 500 °C for 5 min to form the LaTaON film with the sufficient oxidization and reduced oxygen vacancy. Al was thermally evaporated and patterned by lithography as a gate electrode with an area of $7.85 \times 10^{-5}\ cm^2$, followed by a forming-gas (5% H_2+95% N_2) annealing at 300 °C for 20 min to reduce its contact resistance.

High-frequency (HF, 1 MHz) capacitance-voltage (C–V) and gate leakage current density versus gate voltage (J_g–V_g) characteristics of the samples were measured by an HP4284A precision LCR meter and a Keithley 4200-SCS semiconductor parameter analyzer, respectively. X-ray photoelectron spectroscopy (XPS) was used to investigate chemical states and the interfacial quality of the high-k/Ge interface. All electrical measurements were carried out under a light-tight and electrically shielded condition at room temperature.

The LaTaON gate dielectrics with four different Ta contents (from 0 to 45%) were investigated by using XPS analysis. Figure 1(a) is the La 3d spectrum, and two strong peaks at 851.69 eV (La $3d_{3/2}$) and 834.81 eV (La $3d_{5/2}$) are detected. The spin-orbit splitting energy of 16.88 eV is very close to 16.9 eV of La_2O_3/LaON,[12] confirming the formation of La_2O_3/LaON. The spectrum of Ta 4d is shown in Fig. 1(b), in which Ta $4d_{3/2}$ and Ta $4d_{5/2}$ peaks are also detected. The spin-orbit splitting energy is 11.30 eV, which is close to 11.24 eV, indicating the presence of Ta^{5+} from Ta_2O_5/TaON.[13]

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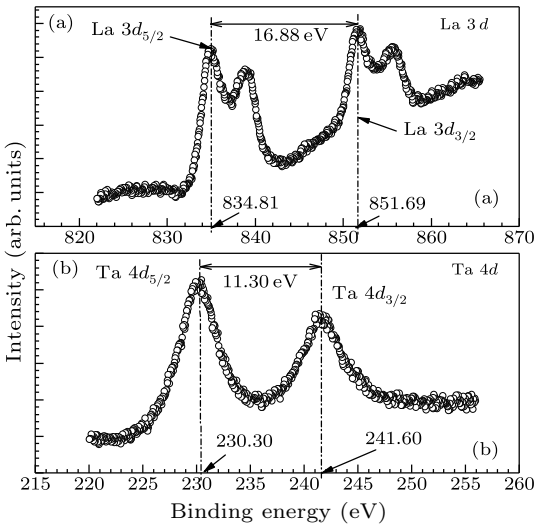

Fig. 1. XPS spectra of LaTaON/Ge MOS with Ta content of ∼15%: (a) La $3d$ and (b) Ta $4d$. Other LaTaON/Ge MOS devices have similar results.

Figure 2(a) shows the spectrum of O $1s$, and its peak at 530.85 eV is very close to that of Ta_2O_5 (530.9 eV) and TaON (530.8 eV),[17] further supporting the presence of Ta_2O_5 and TaON. The N $1s$ spectrum is shown in Fig. 2(b), and its peaks at 394.88 eV and 402.66 eV are in accordance with those of N $1s$ (394.8 eV) and N $3p$ (402.2 eV),[14] verifying N incorporation into the gate dielectric films.

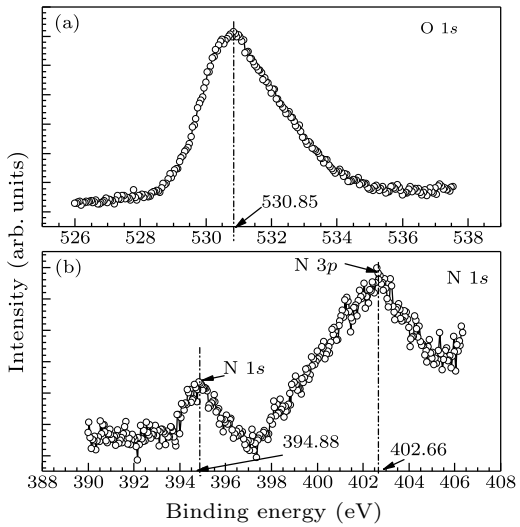

Fig. 2. XPS spectra of LaTaON/Ge MOS with Ta content of ∼30%: (a) O $1s$ and (b) N $1s$. Other LaTaON/Ge MOS devices have similar results.

Figure 3(a) is the spectra of Ge $3d$ and Ta $4f$. Two strong peaks are located at 26.80 eV (Ta_2O_5) and 28.60 eV (Ta $4f_{5/2}$).[14] The 1.8 eV difference between both is very close to the spin-orbit of Ta $4f$ (1.9 eV), indicating the formation of Ta_2O_5[15,16] and TaON[17] again. From the above results, it can be suggested that the LaTaON dielectric film has been formed. By calculating the peak-area ratio of La $3d$ and Ta $4d$ for the three LaTaON samples, their Ta contents [Ta/(Ta+La)] are obtained to be 13.8%, 31.4%, and 42.7%, respectively.

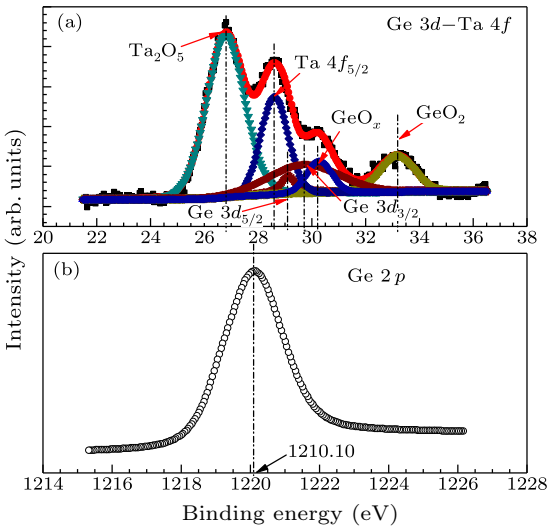

Fig. 3. XPS spectra of LaTaON/Ge MOS with Ta content of ∼30%: (a) Ta $4f$ and Ge $3d$ and (b) Ge $2p$. Other LaTaON/Ge MOS devices have similar results.

The chemical states at the LaTaON/Ge interface can be reflected from Fig. 3. The spectrum of Ge $2p$ is shown in Fig. 3(b). The obvious peak at 1220.10 eV is in good agreement with the banding energy of 1220.2–1220.6 eV for GeO_2.[9] Also, the peak at 33.20 eV is in accordance with the banding energy of GeO_2[14] as shown in Fig. 3(a), which matches with 32.3–33.6 eV of GeO_2.[18–20] The weak peak at 30.20 eV in Fig. 3(a) indicates the presence of GeO_x at the Ge surface.[21] It has been revealed that GeO_2 and GeO_x can form the germanate of $LaGeO_x$/$LaGeO_xN$ when reacting with the La_2O_3/LaON,[11] which is also in accordance with the theory of Dimoulas *et al.*[22] Since the La atom is highly electropositive and La_2O_3 has a lower concentration of oxygen atoms (V_O) (36.4 atom/nm^3) than GeO_2 (41.5 atom/nm^3), the La atoms tend to attract the O atoms in GeO_2 to form a $LaGeO_x$ interfacial layer. The peaks at 29.70 eV (Ge $3d_{3/2}$) and 29.10 eV (Ge $3d_{5/2}$) are obtained from the Ge substrate.[21]

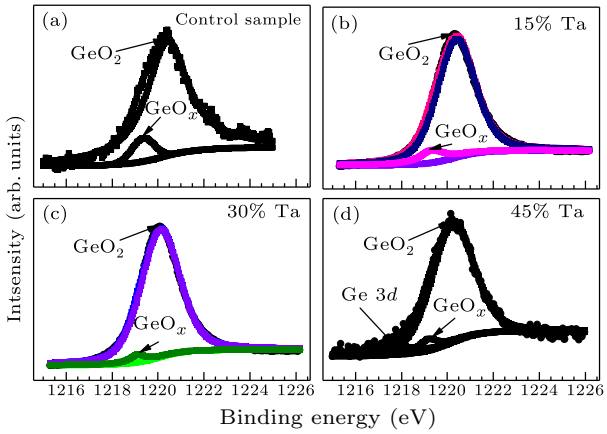

Fig. 4. XPS spectra of Ge $2p$ for four samples: (a) 0% Ta content, (b) 15% Ta content, (c) 30% Ta content, and (d) 45% Ta content.

Because of the spectrum overlap between the Ge $3d$ and Ta $4f$,[14] the Ge $2p$ spectrum from the LaTaON/Ge interface for four samples are shown in

Fig. 4 to further illustrate their interface quality. Obviously, as Ta content increases until 31.4%, the peak area of GeO_x is decreased and then a turnaround is observed for excessive Ta incorporation (42.7%), which indicates that incorporation of a few Ta can suppress the formation of the unstable GeO_x due to its effective blocking role against diffusion of O,[10] and when excessive Ta is incorporated, the interface quality is degraded because of the increased Ge diffusion from the substrate into the interlayer as shown by the Ge 3*d* peak in Fig. 4(d) to enhance the growth of GeO_x.

Figure 5 shows the O 1*s* spectra of four samples to illustrate effects of Ta incorporation on the hygroscopic nature of the LaON. As the Ta content increases, the peak area of La–OH is decreased and the La–O–Ta bond gradually replaces the La–O and La–OH bonds because of the stronger electronegativity of Ta,[10] indicating that incorporation of Ta can indeed improve the hygroscopic nature by suppressing the formation of La–OH. However, as shown in Fig. 5(d), the excessive incorporation of Ta leads to the formation of more La–O–Ge bonds due to diffusion of more Ge into the interlayer, which is in agreement with the results in Fig. 4(d). Therefore, a reasonable-content Ta incorporation into LaON (e.g. ∼30%) is important for achieving a high-quality LaTaON/Ge interface.

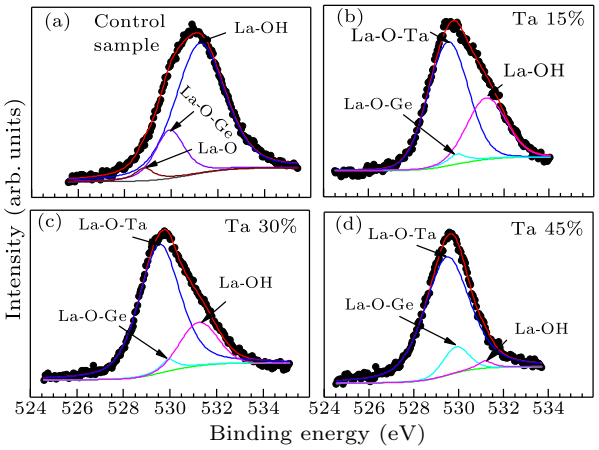

Fig. 5. XPS spectra of O 1*s* for four samples: (a) 0% Ta content, (b) 15% Ta content, (c) 30% Ta content, and (d) 45% Ta content.

Figure 6 presents the typical HF *C*–*V* curves of the control sample (LaON) and LaTaON samples with different Ta contents of 13.8%, 31.4%, and 42.7%. Obviously, as the Ta content increases, the accumulation capacitance (C_{ox}) increases, indicating that the incorporation of Ta into the LaON dielectric can increase its permittivity. The electrical and physical parameters extracted from the HF *C*–*V* curves are listed in Table 1, including C_{ox}, thickness (t_{ox}), and equivalent value (k) of gate dielectric, flat band voltage (V_{fb}), interface-state density near midgap (D_{it}), and gate leakage current density (J_g at $V_g = V_{fb} + 1$, as shown in Fig. 7). The value of V_{fb} is determined by the flat-band capacitance,[23] and D_{it} is estimated using Terman's method.[24] It is observed that as the Ta content increases, D_{it} is decreased firstly, and then increased, indicating that a little of Ta incorporation is beneficial for the improvement of the LaTaON/Ge interfacial properties, and excessive Ta content deteriorates the interface quality, in accordance with the spectrum analysis of Ge 2*p*. In our case, the sample with a Ta content of ∼30% exhibits the best interfacial properties (the smallest D_{it}). Compared with the results in Ref. [11], we obtain a higher k value of 22.46 (versus 21.0), a lower gate leakage current density of 8.32×10^{-5} A/cm^2 (versus 3.07×10^{-4} A/cm) at $V_g = V_{fb} + 1$, and a comparable D_{it} of 7.6×10^{11} cm^{-2} eV^{-1} (versus 6.76×10^{11} cm^{-2} eV^{-1}).

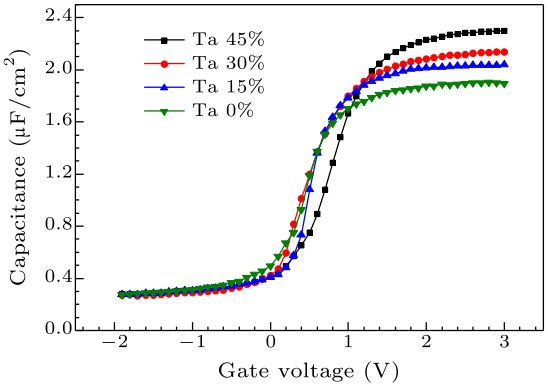

Fig. 6. Typical HF *C*–*V* curve of four samples with different Ta contents.

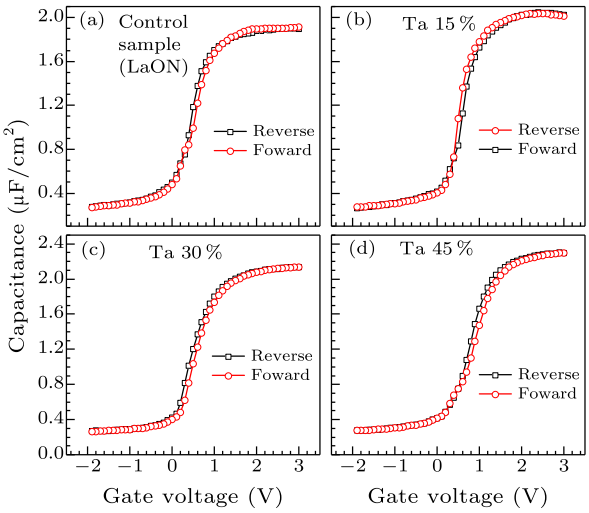

Fig. 7. Hysteresis of *C*–*V* curves for four samples: (a) 0% Ta content, (b) 15% Ta content, (c) 30% Ta content, and (d) 45% Ta content.

Figure 7 shows hysteresis of the *C*–*V* curves for the four samples, swept in two directions (from inversion to accumulation and then back). All the samples exhibit small hysteresis voltages. To quantify their differences, the hysteresis voltage is calculated as an averaged hysteresis from 0 to 2 V. The hysteresis voltages of the four samples are found to be 32, 27, 23, and 38 mV with the increasing Ta content. Obviously, the

sample with a Ta content of 30% shows the smallest hysteresis, in accordance with its lowest D_{it}, supporting its best interfacial and bulk qualities of the gate dielectric.

Table 1. Electrical and physical parameters extracted from the HF C–V curve.

LaTaON	C_{ox} (pF)	t_{ox} (nm)	k	D_{it} (10^{12} cm^{-2} eV^{-1})	V_{fb}	J_g (A/cm^2) @$V_g = V_{fb} + 1$
Ta (0%)	149.5	10	21.51	2.03	0.16	3.31×10^{-3}
Ta (15%)	159.9	9.4	21.63	1.69	0.35	3.47×10^{-3}
Ta (30%)	167.8	9.3	22.46	0.76	0.23	8.32×10^{-5}
Ta (45%)	180.6	9.1	23.65	1.89	0.42	1.91×10^{-3}

The frequency dispersion of C–V curves for the four samples is shown in Fig. 8 to further illustrate their interface quality. The dispersive behavior of the C–V curve from depletion to accumulation and from weak to strong inversion is attributed to the interface traps near the Ge valance band and conduction band, respectively.[25] The sample with a Ta content of ∼30% exhibits the smallest frequency dispersion in the two regions, suggesting the smallest D_{it}, as shown above.

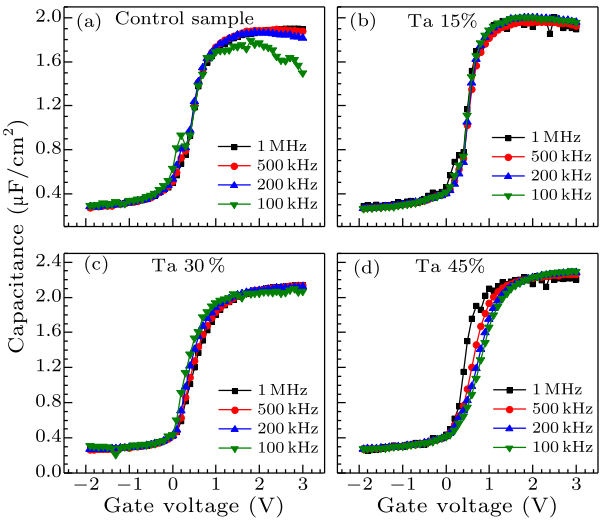

Fig. 8. Frequency dispersion of C–V curves for four samples: (a) 0% Ta content, (b) 15% Ta content, (c) 30% Ta content, and (d) 45% Ta content.

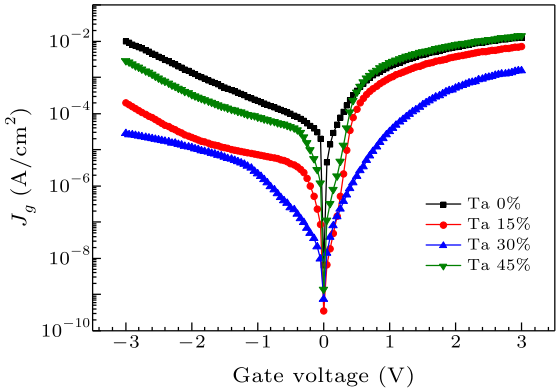

Fig. 9. Gate leakage current density versus gate voltage for the four samples.

Figure 9 shows typical gate-leakage properties of the four samples. Obviously, the sample with a Ta content of 30% exhibits the lowest gate leakage current. At $V_g = V_{fb} + 1$, J_g is 3.31×10^{-3}, 3.47×10^{-3}, 8.32×10^{-5}, and 1.91×10^{-3} A/cm^2 for the four samples with Ta contents of 0%, 15%, 30%, and 45% (as listed in Table 1), respectively, corresponding to their respective interfacial qualities.

In addition, the AFM images of the gate-dielectric surface of the four samples are shown in Fig. 10. It can be seen that all the samples show a relatively smooth surface, and the root-mean-square (rms) values of their surface roughness are 0.283, 0.264, 0.222, and 0.228 with increasing the Ta-content, respectively. Obviously, the samples with Ta contents of 31.4% and 42.7% exhibit less roughness relative to the other two samples. The latter is due to LaON readily forming low-density $La(OH)_3$[11] when moisture absorption happens, which deteriorates its surface roughness. Therefore, it can be concluded that the Ta incorporation can improve the hygroscopic nature of LaON, and the sample with reasonable Ta content (e.g. ∼30%) could obtain the least roughness and thus the best interface quality.

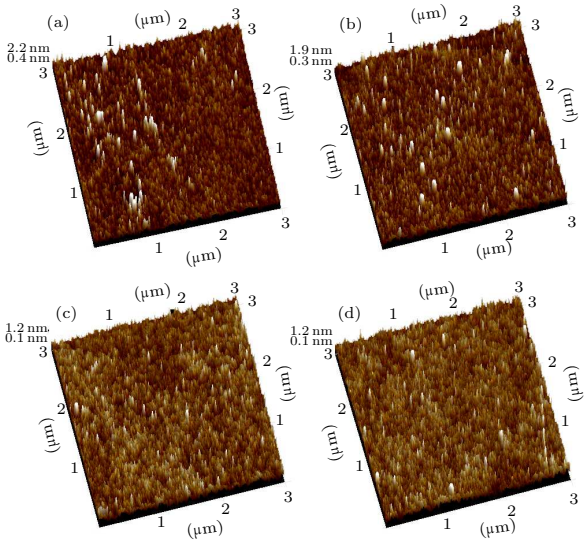

Fig. 10. AFM image of the gate dielectric of the four samples: (a) 0% Ta content, (b) 15% Ta content, (c) 30% Ta content, and (d) 45% Ta content.

In summary, the effects of the Ta content in LaTaON gate dielectric on the interfacial and electrical properties of the Ge MOS capacitor have been in-

vestigated. Experimental results show that reasonable Ta incorporation in LaON (e.g. Ta content of ∼30%) can improve the LaTaON/Ge interfacial and electrical properties of Ge MOS capacitor, but the opposite effect is obtained when excessive Ta is incorporated. This is because incorporation of suitable-content Ta can suppress the formation of the unstable GeO_x due to its blocking role against diffusion of O and improve the hygroscopicity of LaON; however, excessive Ta incorporation results in the diffusion of more Ge into the interlayer to degrade the interface quality. XPS analyses indicate that the least GeO_x exists at the Ge surface for the sample with a Ta content of ∼30%, attributed to its good trade-off between the suppression of GeO_x and Ge diffusion. Therefore, it is expected that LaTaON with a suitable Ta content could be directly used as the gate dielectric of Ge MOS devices to achieve excellent interfacial and electrical properties of devices.

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