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The interfacial mixing of silicon coatings on niobium metal: a comparative study

P. D. Stupik*, M. M. Donovan and A. R. Barron†
Department of Chemistry and Materials Research Laboratory, Harvard University, Cambridge, MA 02138 (U.S.A.)

T. R. Jervis and M. Nastasi
Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545 (U.S.A.)

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Abstract

Graded interfaces between niobium substrates and evaporated silicon films were obtained through thermal annealing, ion-beam mixing and laser mixing. The samples were characterized with Rutherford backscattering, Auger electron spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy and X-ray diffraction. Thermal annealing was found to produce asymmetric interfacial gradients, while ion-beam and laser treatment produced symmetric gradients. Samples were subjected to heating in dry oxygen at 650 °C in order to study the thermal oxidation stability of the coatings. The amorphous laser-mixed, then ion-beam treated samples were found to be resistant to severe oxidation. It was concluded that a smoothly graded interfacial region will be stable with respect to thermal and lattice mismatch; but if the mixed zone is crystalline, grain-boundary oxidation occurs.

1. Introduction

New heterophase materials are extremely important for high temperature aerospace applications [1, 2], in particular, oxidation- and corrosion-resistant coatings of niobium and its alloys [3]. While the performance of heterophase materials is determined by many factors, adhesion at the heterophase interface is one of the most important. Three factors that affect adhesion are chemical bonding, microstructure and thermal characteristics of the interface. The nature of the chemical bonding at the interface will determine the intrinsic mechanical properties, and in this regard we are presently exploring the relationship between the chemical bonding and the intrinsic properties of the interface *via* the use of the layer Korringa–Kohn–Rostoker (LKKR) technique and model cluster calculations [4]. Equally important in determining the adhesion of the interface are microstructural properties, for example the degree of epitaxy and lattice mismatch. Finally, the thermal stability of the interface during high temperature cycling will be determined by the dissimilarity of the materials thermal expansion coefficients. The present work attempts to address the problems of lattice and thermal coefficient mismatch through the formation of a graded interfacial region.

A graded interface shows a smooth variation in atomic concentrations, with the possibility of a constant composition or constant phase region. Since the microstructure present at the interface will be process dependent, we have explored three different methods for the creation of gradients between niobium and silicon: thermal, ion-beam and laser treatments. Although it is known that niobium silicides, *per se*, have insufficient oxidative stability as protective coatings for niobium and its alloys [5], the Nb/Si system has been extensively characterized for semiconductor applications, making it a useful model for these studies.

2. Experimental procedures

Elemental silicon (99.999%) was deposited by electron-beam evaporation (background pressure $< 10^{-5}$ Torr) onto 2 mm thick polished niobium (+99%) substrates [6]. The substrates were sputtered with argon ions prior to and during the early stages of deposition to prevent the formation of native niobium oxide at the interface. The deposition rate was increased from 0.5 to 2.0 Å s^{-1} during the run. The thickness of the coating (between 1800 and 2000 Å) was determined by Rutherford backscattering (RBS). One sample, A, was retained untreated while the

* Present address: Corion Corporation, Holliston, Massachusetts 01746, U.S.A.
† Author to whom correspondence should be addressed.

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remainder, B–O, were subjected to the following treatments.

Three samples were heated under vacuum ($< 3 \times 10^{-5}$ Torr) in a quartz tube furnace, to induce diffusion and silicide formation. Sample B was heated for 18 h at 550°C. Sample C was subjected to a two-step anneal at 550 °C and 850°C, 4 h each step, while sample D was treated in a similar fashion to C, but for 18 h each step.

Five samples were subjected to ion-beam mixing with 400 keV Ar^+ ions at a pressure below 2×10^{-7} Torr. The samples were given a total dose of 3×10^{16} ions cm^{-2} which took a total of 20 min each. Samples E, F and G were ion-beam mixed at room temperature after which F was ion-beam mixed at 78 K while G was thermally annealed at 300 ° C. Samples H and I were mounted on a hot stage and ion-beam mixed at 300 °C. As with F sample I was then mixed for a further 20 min at 78 K.

Samples J–O were treated in air with 248 nm light from an excimer laser. Since the output of excimer lasers is spatially non-uniform, a multi-element beam homogenizer was used. This device produces a square output pattern with a spatial uniformity of better than 90% on the sample surface. The samples were translated continuously in front of the laser beam at a speed which corresponds to five pulses in each location, further averaging the fluence incident on the sample. A fixed spot size was used but different pulse energies produced fluences of 0.5 (J, K), 1.7 (L, M) and 2.5 (N, O) J cm^{-2} respectively. The laser repetition rate was 5 Hz, allowing the sample ample opportunity to return to ambient temperature between pulses (the initial cooling rate is of the order of 10^9 K s^{-1}). Following laser mixing, samples K, M and O were ion-beam mixed at 78 K with a dose of 3×10^{16} Ar^+ ions cm^{-2}.

The coatings were characterized by Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and low-angle X-ray diffraction (XRD). RBS was carried out using a 2.0 MeV He^+ ion beam from a Tandem accelerator at the Los Alamos National Laboratory. AES was carried out on a Perkin–Elmer SAM-660. XPS spectra were acquired with a Surface Science Laboratories Model SSX-100 spectrometer with a monochromatized Al Kα X-ray source (10^{-8}–10^{-9} Torr). SEM studies were performed on a JEOL JSM-35 scanning microscope. A Rigaku thin film diffractometer was used for low-angle XRD studies.

Oxidation studies were carried out under a dynamic atmosphere of dry O_2 (UHP Grade) in a quartz tube, using a Lindberg furnace.

3. Results

3.1. Thermal mixing (B–D)

Samples B, C and D were thermally annealed as described in Section 2, after which the surfaces were coloured: B blue, C and D purple. The SEM showed no significant variation in surface morphology between the thermally annealed samples and the untreated sample A.

The Auger sputter depth profiles of samples A, B, C and D are shown in Fig. 1. The etching rate for all the depth profiles is *ca.* 88 Å min^{-1} for the silicon overlayers; however, lower rates are undoubtedly observed for the

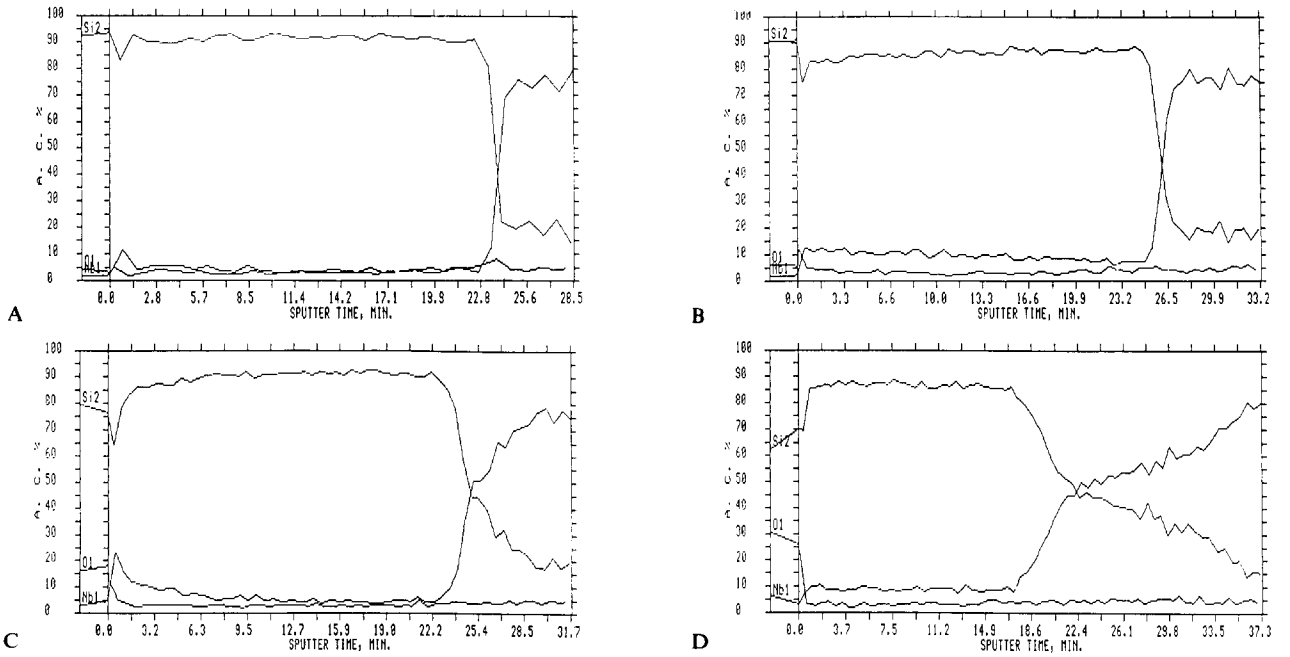


Fig. 1. AES depth profiles of as-deposited and thermally annealed silicon layers on niobium substrates: A, untreated; B, 550 °C (18 h); C, 550 °C (4 h) and 850 °C (4 h); D, 550 °C (18 h) and 850 °C (18 h).

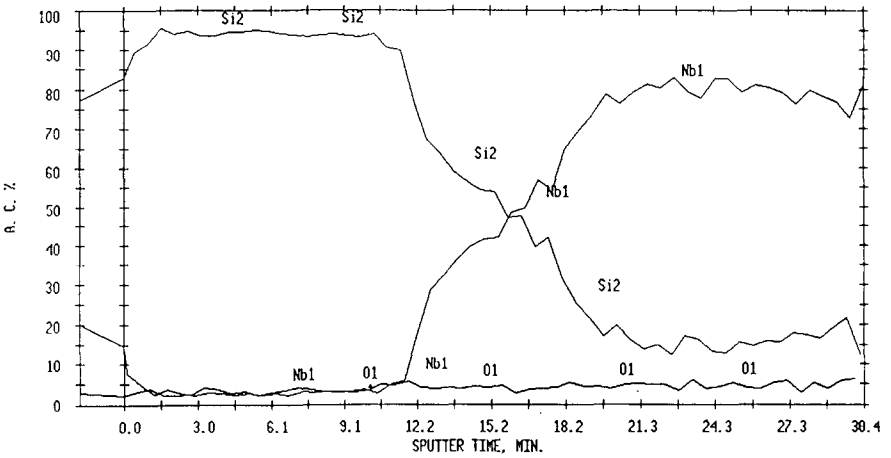
mixed phases. The slightly broadened interfacial region in the low temperature (550 °C) annealed sample, B, compared with the untreated sample, A is consistent with the previously noted slow diffusion of silicon into niobium at temperatures below 650 °C [7]. Sample C (Fig. 1(c)) not only shows a more pronounced diffusion region but possibly a narrow region (*ca.* 50 Å) of constant composition, possibly due to the formation of a silicide phase. The formation of such a phase could not, however, be confirmed by XRD. The constant composition region in sample D is much broader (*ca.* 700 Å) than in C consistent with the increased anneal times. In addition to the very broad silicon diffusion tail into the niobium, significant diffusion of niobium into silicon is observed [8]. Unlike C, the formation of $NbSi_2$ in D is confirmed *via* XRD, by comparison with standard powder data files [9]. In addition, peaks due to crystalline silicon were also observed. Not surprisingly, the X-ray pattern of the as-deposited sample (A) showed only substrate reflections indicating the amorphous nature of the silicon coating. XPS results show unreacted silicon overlayers in all cases.

3.2. Ion-beam mixing (E–I)

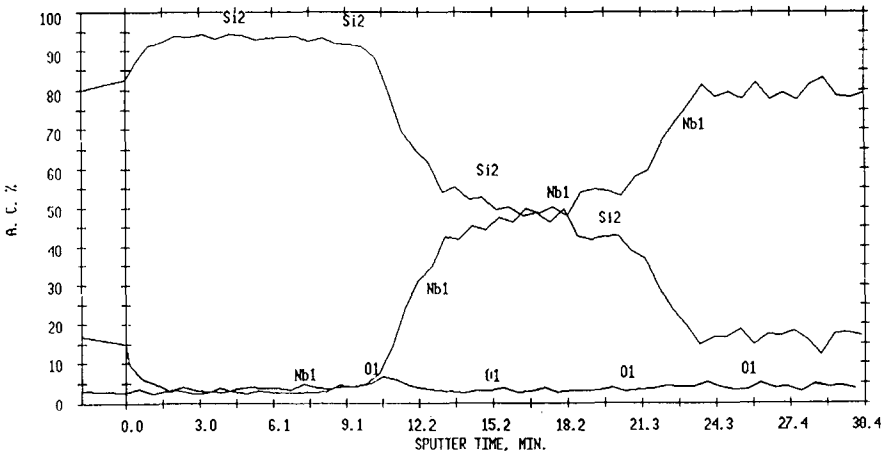
The AES sputter depth profiles (Fig. 2) and RBS spectra (Fig. 3) clearly show the effect of ion-beam mixing at 300 °C compared with room temperature (RT). An important difference between the ion-beam mixed samples and those thermally annealed is the prominent diffusion of niobium into the silicon, towards the surface in the former.

The room temperature mixed sample, E, shows a broad (*ca.* 600–700 Å) amorphous interfacial gradient with no apparent zone of constant composition [10]. In contrast to E, sample H has a mixed layer with a rather constant composition corresponding to Nb:Si ratio of 1. From XRD this constant composition region appears to consist of both Nb_5Si_3 and $NbSi_2$ [9, 11]. Subsequent ion-beam treatment of H at 78 K (I) showed no change in the Auger depth profile, but the XRD showed the silicide region to be amorphous.

It should be noted that thermally annealing the RT ion mixed samples at 300 °C (G) showed no further mixing by AES or silicide formation by XRD [12]. In addition to the



E



H

Fig. 2. AES depth profiles of ion-beam treated silicon layers on niobium substrates: E, room temperature; H, 300 °C.

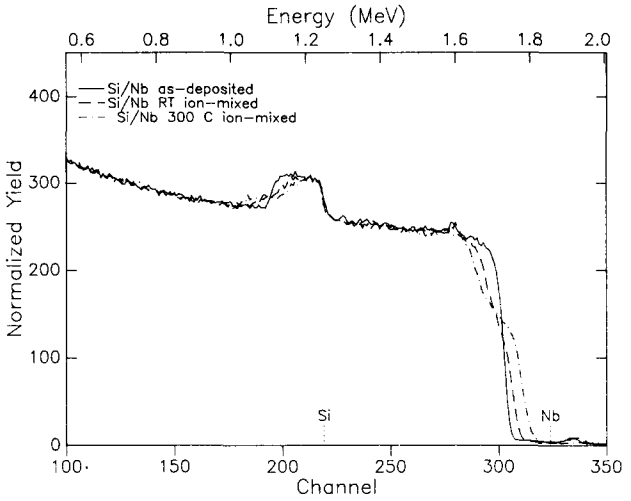


Fig. 3. RBS spectra of the ion-beam mixed samples. E (room temperature) and H (300 °C), as compared with the as-deposited sample A.

interfacial mixing between niobium and silicon the surface Si_{2p} XPS spectra of the ion-beam treated samples shows the formation of a silicon suboxide at the surface and diffusion of oxygen into the silicon.

3.3. Laser mixing (J–O)

The RBS spectra of the laser mixed samples J, L and N are shown in Fig. 4 along with that for the as-deposited sample A. Sample J mixed with 5 pulses at a fluence of 0.5 J cm^{-2} shows a comparable amount of mixing to the 300 °C ion-beam mixed case (H), but with no obvious constant composition region. By contrast, the samples mixed at 1.7 J cm^{-2} (L) and 2.5 J cm^{-2} (N) show substantial mixing as well as regions of constant

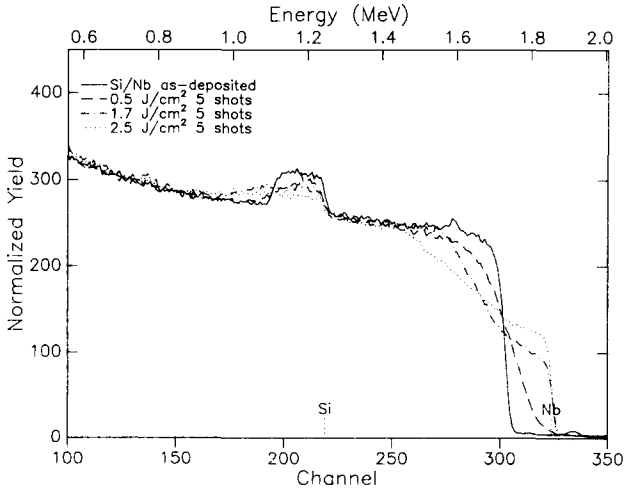


Fig. 4. RBS spectra of the laser mixed samples, H (0.5 J cm^{-2}), L (1.7 J cm^{-2}) and N (2.5 J cm^{-2}) as compared with the untreated sample, A.

composition [13, 14]. A fit to the RBS data in the latter two cases is consistent with layers of $NbSi_2$ approximately 2000 Å and 3000 Å thick respectively with a graded interface to the underlying niobium. In both these samples, niobium has diffused to the front surface of the samples. The identity of the mixed zones as $NbSi_2$ is confirmed by XRD [8].

Auger depth profile analysis of sample L, shown in Fig. 5, is consistent with the analysis of the RBS results given above. Through the mixed zone the ratio of silicon to niobium is approximately constant. Further, the interfacial region is smoothly graded over a distance of about 800 Å.

The samples that were ion-beam treated at 78 K after being laser mixed, K, M and O, show no change in the AES and RBS spectra; however, the XRD shows that the coating is essentially amorphous.

3.4. Oxidation studies

All the samples were subjected to heat treatment at 650 °C in dry oxygen for 30 min per run. The silicon coating of samples A and B was completely oxidized and interfacial failure occurred, completely detaching the silicon overlayer. Subsequent XPS analysis of the surface showed only oxygen and niobium signals. Although samples C and D showed significant oxidation, interfacial failure did not occur at the Si/Nb interface. The remaining layer of silicide was retained even after several oxidation cycles.

The silicon overlayer of the samples ion-beam mixed at room temperature (E–G) remains essentially intact after oxidation. The presence of localized pitting and oxidation, due to the presence of pinholes in the deposited film, can be seen from the SEM micrograph (Fig. 6). There is no significant difference in thermal oxidative stability of the niobium silicon interface for any of the room temperature ion mixed samples.

The oxidation of samples H and I, mixed at 300 ° C, results not only in the catastrophic failure of the Nb/Si interface but extensive oxidation of the niobium substrate. In fact, oxidation of the niobium in these samples is more severe than in either sample A or uncoated niobium metal.

The amorphous laser mixed then ion-beam treated samples, K, M and O, are resistant to severe oxidation, despite pitting due to pinholes, for several thermal cycles. Their non-ion-beam treated polycrystalline counterparts oxidize more rapidly.

4. Discussion

Previous work has shown that niobium silicides may be prepared by the thermal, ion-beam and laser treatment of niobium silicon multilayers; however, no assessment has

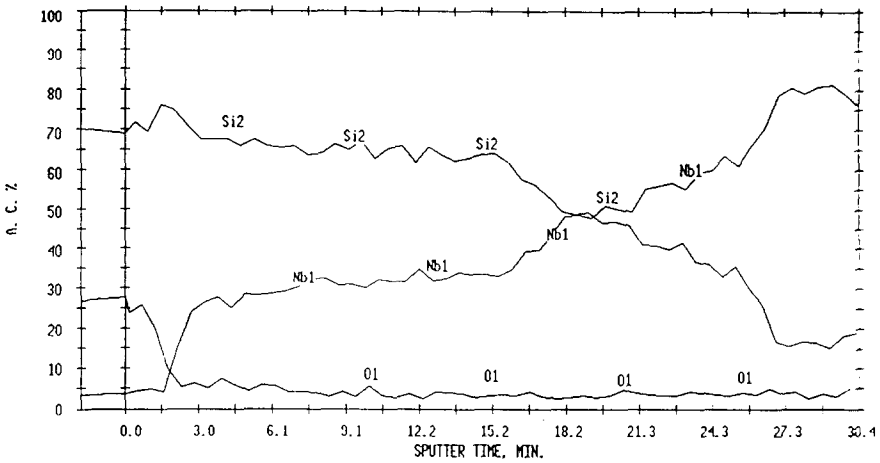


Fig. 5. AES depth profile of sample L (laser mixed at 1.7 J cm^{-2}).

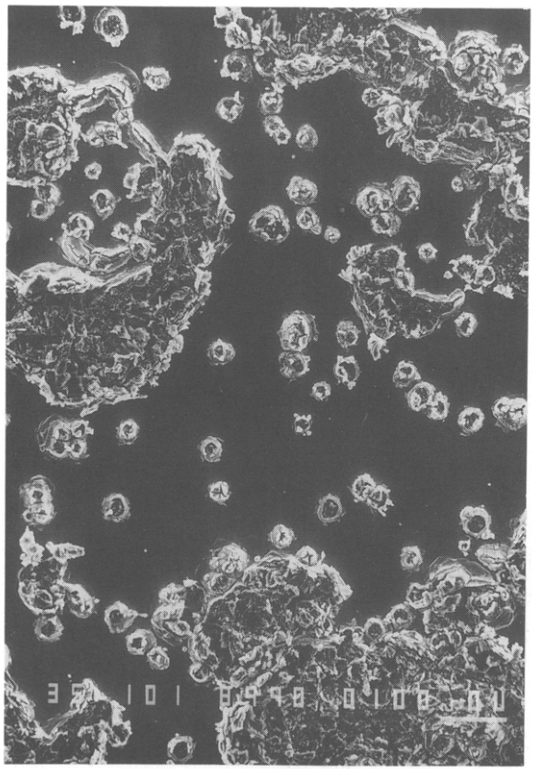


Fig. 6. The SEM micrograph of the room temperature ion-beam mixed sample, E, after oxidation, shows that although the silicon overlayer is largely unaffected, pitting, in which Nb_2O_5 is present, has occurred due to the presence of pin holes in the original film.

been made of the effectiveness of each technique for the formation of a thermally robust interface between these two dissimilar materials. In the present study all the mixing techniques explored have been successful in producing a graded interfacial region between niobium and silicon.

Thermal annealing is singular in the formation of an asymmetrical gradient (Fig. 1(d)), in which the silicon overlayer shows significant diffusion into the niobium substrate. The niobium does not appear to diffuse thermally as readily as silicon. The result is therefore a sharp interface between the unreacted silicon and the mixed region. In contrast the interface between the mixed region and the niobium substrate has a smooth gradient of composition over *ca.* 200 Å. It is at the sharp silicon–mixed phase interface that mechanical failure under oxidative heating occurs, while the smoothly graded interface that remains is stable to further oxidative heating.

By contrast with the results obtained for thermal mixing, symmetrically graded interfacial regions are produced with both ion-beam and laser mixing. Despite these smooth gradients, mechanical failure does occur for some samples under oxidation. This is undoubtedly related not to any lattice mismatch or difference in thermal expansion but to the extent of epitaxy at the interface. For example: oxidation occurs for the 300 °C ion-beam mixed sample which, from XRD, has a crystalline interfacial region, whereas no significant oxidation occurs for the room temperature mixed samples in which the mixed region is amorphous. In a similar manner the laser mixed samples are oxidized but those receiving an additional mixing ion-beam treated at 78 K, that is with an amorphous region, are stable. Thus a smoothly graded interfacial region will be stable with respect to thermal and lattice mismatch, but if the mixed zone is crystalline oxidation may occur within the grain boundaries. In this case we propose that the crystal size will affect the resistance of the mixed region to oxidation. We further conjecture that the stable thermally mixed region which remains after oxidation of the unreacted silicon overlayer will have larger crystal grain size, than the laser mixed samples, where the rapid cooling rate will

favour small grains. It should be noted, however, that laser processing in general leads to a wide range of microstructures, from amorphous phases to epitaxial growth, making it difficult to predict the stability of the mixed interface.

One surprising result of these studies is that oxidation of the 300 °C ion-beam mixed sample, H and I, results in enhanced corrosion of the niobium substrate when compared with the untreated sample A, and even uncoated niobium. This result would suggest that the high temperature ion-beam mixing process either provides the initial route for oxidation into the bulk perhaps by knock-on oxygen incorporation or causes more structural damage to the niobium substrate than previously considered.

Acknowledgments

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