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Probing the growth, structure, and magnetism of epitaxial films by grazing scattering of fast ions

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Abstract

Techniques based on grazing scattering of keV light ions to study ultrathin epitaxial films are presented. A key feature of these techniques is an extreme sensitivity to morphology, elemental composition, and magnetic properties of the topmost atomic layer of the films, as demonstrated by recent experiments on Cr, Mn, Fe, and Ir films grown on magnetized Fe(1 0 0) substrates. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Trajectories of fast ions impinging under grazing angles upon an atomically smooth crystal surface are determined by a series of correlated small-angle deflections with surface-layer atoms. The ions do not penetrate into the bulk, but are specularly reflected in front of the surface. By analogy with channeling in bulk crystals [1], this phenomenon has been called "planar surface channeling".

Soon after the experimental realization of surface channeling [2], grazing ion-surface scattering has been applied in studies on magnetism of crystal surfaces by Rau and Sizmann [3]. In these experiments, the long-range magnetic order at Ni surfaces has been studied by grazing scattering (0.4° incidence angle to the surface plane) of 150 keV D^+ ions. The spin polarization of electrons captured during scattering into the ground term of deuterium atoms is detected via an analysis of a subsequent nuclear reaction. A key feature of this technique is an extreme surface sensitivity, because the (final) capture process occurs at distances well above the surface layer.

For molecular beam epitaxy (MBE) and related techniques to grow smooth films on crystalline substrates, use of grazingly scattered ions offers interesting features to probe properties of ultrathin films:

1. The collision geometry does not interfere with deposition sources or other components for diagnostics (e.g. electron analyzers) at normal incidence.

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2. In situ and real-time measurements are feasible, which is appropriate considering the nonequilibrium character of MBE growth.
3. There are virtually no restrictions concerning the choice of experimental parameters like growth temperature, deposition rate, film-substrate combination, or ambient-gas pressure.

An analysis of angular distributions of reflected ions or appropriate ion-induced electronic excitations yields information on structural, chemical, electronic, and magnetic properties of films. Common to these techniques is an extreme surface sensitivity, ensured by the peculiar ion trajectories and the local character of excitations owing to the effective dynamical screening of the ion potential [4]. This is an important advantage in ultrathin-film studies over established techniques averaging over some atomic layers beneath the surface.

In this paper, we briefly review various grazing ion-scattering techniques developed to study growth, structure, and magnetism of ultrathin epitaxial films. The techniques are illustrated by recent experiments performed for transition metal (Cr, Mn, Fe, Ir) films on magnetized Fe(1 0 0) substrate surfaces, using an experimental setup as sketched in Fig. 1.

2. Growth and morphology

The correlated scattering process in surface channeling is perturbed by structural irregularities like edges of islands nucleated on the surface during epitaxial growth. This leads to off-specular reflection. As proposed by Mannami et al. [5] in 1988, the periodic change in surface morphology in case of a two-dimensional (2D) or layer-by-layer growth results in oscillations of the specular-beam intensity, whereas three-dimensional growth causes the intensity to decrease monotonically. Fujii et al. [6,7] observed intensity oscillations during homoepitaxial growth on semiconductors. The oscillations are explained by a simple "optical model", where ions are scattered from a hard-wall repulsive potential following the mesoscopic surface contour. Oscillations in heteroepitaxial growth of metal films were found by Igel et al. [8–10]. Based on computer simulations of ion trajectories, detailed information on the morphology

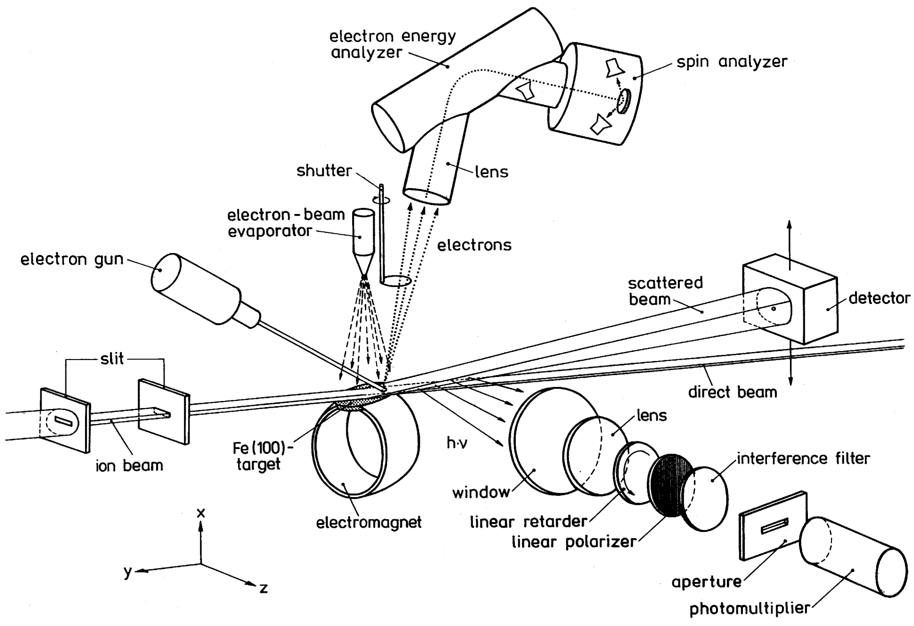

Fig. 1. Sketch of our experimental setup.

of the growing surface (e.g. 2D island density) could be derived. A good description of experiments on metal homoepitaxy can be achieved by combining trajectory simulations with Monte Carlo simulations of growth, as demonstrated by Langelaar and Boerma [11]. DeLuca et al. [12,13] and Pfandzelter et al. [14] have extended the technique by exploiting its real-time capabilities to study monomer diffusion and recovery phenomena.

In contrast to established techniques based on diffraction like RHEED, grazing ion-surface scattering is a real-space technique which can be described by concepts of classical mechanics. This facilitates the interpretation of data. In an extension of the optical model, Labanda and Barnett [15] quantified the technique in terms of cross-sections for scattering at monomers and step edges of islands. This step-density model seems to be appropriate at small densities where shadowing effects and the correlated nature of the scattering process are of minor importance. These latter effects were included in a computational study by Pfandzelter [16] based on a stochastic model for the growing film, which shows that the relevant quantity is the pair correlation of surface-layer atoms rather than the step density.

An example for specular-beam intensity oscillations is shown in Fig. 2, where 25 keV He^+ ions are grazingly scattered during homoepitaxial growth on Fe(1 0 0) [14]. Pronounced oscillations over an extended range of deposition times are observed at 550 K, indicating almost perfect layer-by-layer growth with a film surface nearly as smooth as the pristine Fe surface (mean distance between surface steps >1000 Å). The strong decay of the signal at 300 K points to a large density of nucleation sites. At high temperatures (630 K), the signal hardly changes upon deposition, indicating step-flow growth. Here growth proceeds by step propagation and the surface morphology remains constant.

Temperature-dependent 2D island densities deduced from these data are compared in Fig. 3 with results obtained from scanning tunneling microscopy by Stroscio et al. [17]. Based on nucleation theory [18,19], we infer from an Arrhenius dependence below about 500 K a monomer diffusion barrier of $E_d = 0.485 \pm 0.050$ eV. The strong

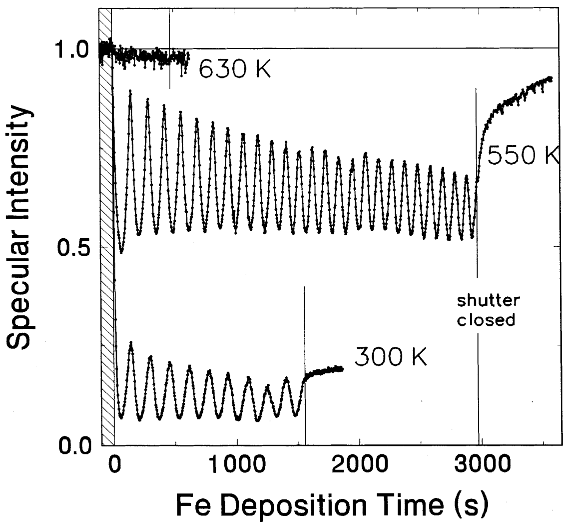

Fig. 2. Specular intensity (normalized) for 25 keV He^+ ions grazingly scattered during growth of Fe on Fe(1 0 0) at the indicated temperature. The vertical lines indicate the opening and closing of the shutter, respectively. The maximum film thickness deposited at 630 K is about 3.2 ML.

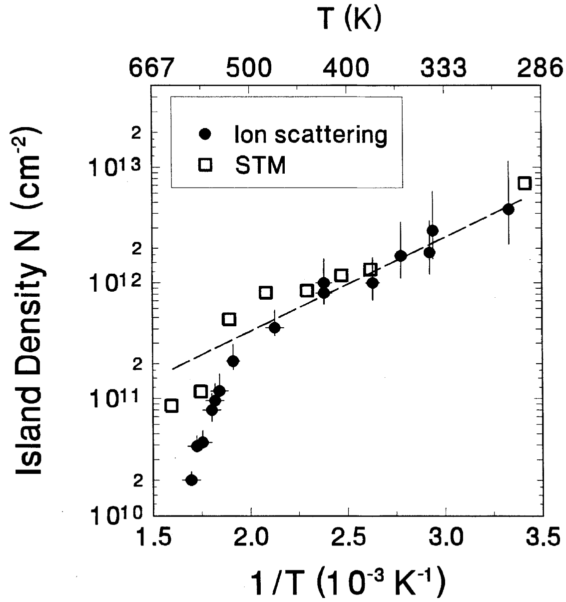

Fig. 3. Arrhenius plot of saturation island densities obtained from the specular intensity of grazingly scattered 25 keV He^+ ions (solid circles). The line is a fit to the data for $T \leqslant 470$ K. Open squares show STM results from [17].

decrease in island density at higher temperatures indicates an increase in critical cluster size [14,18,19].

3. Chemical composition

Structures formed during film growth are often metastable and a quasi-equilibrium is established by interfacial alloying between film and substrate material [20], which, in the end, determines the physical properties of the film. Standard diagnostics for elemental compositions of films, like electron-induced Auger electron spectroscopy (AES) average over several layers beneath the surface. This is not adequate for ultrathin films with possibly large gradients in layer-dependent elemental concentrations.

As proposed by Pfandzelter and Lee [21,22] and Rau et al. [23,24], the surface sensitivity of AES can be enhanced significantly by using grazingly incident ions instead of electrons as primary particles. The ions do not penetrate and the probing depth is restricted to the topmost surface layer, irrespective of the escape depth or inelastic mean free path of Auger electrons. This has been demonstrated in an overlayer experiment for proton-induced AES by Pfandzelter and Landskron [25], where one monolayer (ML) of Ag on Cu(1 1 1) almost quenches the substrate Auger signal.

Crucial for an application of the technique is a proper choice of scattering conditions. Creation of Auger electrons via inner-shell ionization requires close-encounter collisions which, in a sense, counter the gist of channeling. The sort of ions, beam energy and incidence angle thus have to be chosen by means of computer simulations, in order to achieve both a high signal and a high surface sensitivity [26].

In contrast to another topmost-layer probe in AES, positron annihilation [27], grazing ion-scattering hardly faces restrictions concerning the choice of Auger transition and should allow, within limits, for a depth profiling by varying the ion-beam incidence angle. Alternatively, this can be achieved by simultaneously measuring electron-induced signals, possibly for different Auger transitions with different probing depths. This way, concentration profiles with near monolayer depth resolution can be obtained, as has been demonstrated for Cr/Fe(1 0 0) [28].

Fig. 4 shows Fe Auger signals induced by 25 keV protons grazingly scattered during growth of Ir on Fe(1 0 0) (solid circles) [29]. Whereas low growth temperatures (Fig. 4(b)) cause a monotonic decrease of the substrate signal as expected for overlayer growth, the signal remains constant for high-temperature growth (Fig. 4(a)). This shows, without the need for a complicated analysis, that

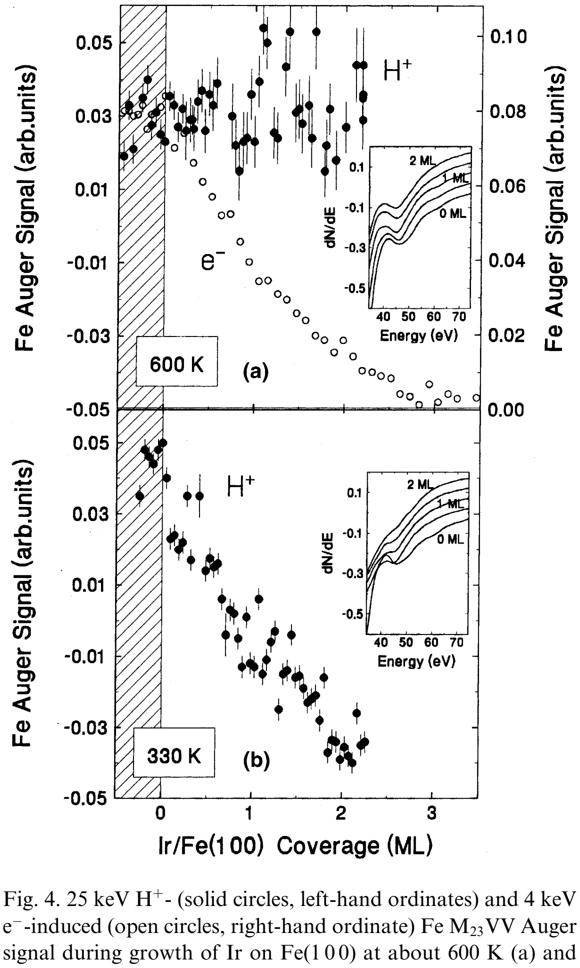

Fig. 4. 25 keV H^+- (solid circles, left-hand ordinates) and 4 keV e^--induced (open circles, right-hand ordinate) Fe $M_{23}VV$ Auger signal during growth of Ir on Fe(1 0 0) at about 600 K (a) and 300 K (b), respectively. The signals are evaluated from differentiated spectra dN/dE (see insets). The vertical lines indicate the opening of the shutter. Insets: dN/dE spectra (H^+-induced) for Ir coverages of 0, 0.6, 1, 1.5, and 2 ML (for clarity, the origins are displaced vertically by constant amounts).

the Ir film is terminated by Fe atoms. Note that this feature is not present in electron-induced signals (open circles).

4. Magnetic order

4.1. Spin-polarized electron capture

As mentioned in Section 1, grazingly scattered ions can be used as probes for the long-range magnetic order at a surface by measuring the spin polarization of captured electrons. As an alternative to the technique of deducing the spin polarization from a nuclear reaction [3], Winter et al. [30,31] measured the polarization of fluorescence light emitted after capture into excited atomic states of the projectile. This "optical" version of the technique has practical advantages owing to a simple setup, reasonably high signals, and a wide choice of projectiles and beam energies.

This technique is sensitive to a region above the topmost surface layer, because excited atomic states can only survive for distances from the surface exceeding the mean radii of corresponding electronic orbitals. Similar to other diagnostics for surface magnetism, a quantitative analysis of experimental data is difficult. Although the spin polarization P of captured electrons can be derived in a straightforward manner from the observed degree of circular polarization of the emitted light [32], a theoretical treatment of the formation of excited atomic terms under consideration of a realistic spin-resolved target band structure has not been worked out so far. Nevertheless, experimental studies on bulk crystal surfaces (e.g. on the target-temperature dependence of spin polarizations) [30,31,33–36] give evidence that P reflects sign and magnitude of the spin part of the net magnetic moment at the surface.

The technique is ideally suited to study heteroepitaxy of transition metals, where interlayer exchange coupling phenomena give rise to complex layer-dependent magnetic configurations [37]. An example is shown in Fig. 5, where Mn films are grown on a magnetized Fe(1 0 0) surface [38]. As inferred from the oscillations in the intensity of reflected ions (Fig. 5(a)), growth proceeds in a

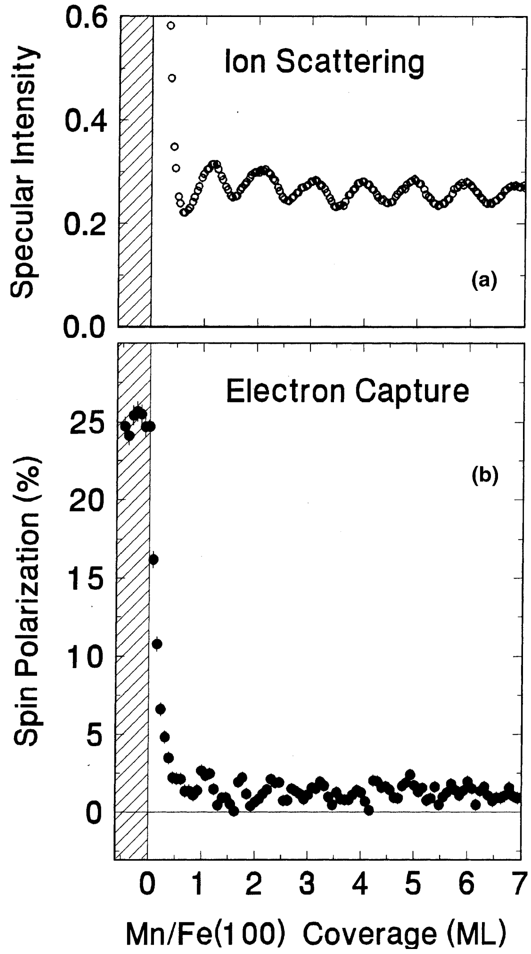

Fig. 5. (a) Specular intensity of 25 keV H^+ ions grazingly scattered during growth of Mn on Fe(1 0 0) at 300 K (normalized to the value for the uncovered surface). The vertical line indicates the opening of the shutter. (b) Spin polarization of fluorescence light emitted in the HeI $1s2s^3S$–$1s3p^3P$, $\lambda = 388.9$ nm transition after electron capture by 25 keV He^+ ions.

layer-by-layer mode at 300 K. The magnetic order at the film surface is studied via grazing scattering of 25 keV He^+ ions and detecting the polarization of light of the HeI $1s2s^3S$–$1s3p^3P$ transition after electron capture. The spin polarization of the captured electrons shows a pronounced decay from the uncovered Fe surface value (25%) to a small, almost constant value of $2\% \pm 2\%$ (Fig. 5(b)). In the submonolayer coverage range, this is in accordance with a parallel alignment of Mn magnetic moments with an opposite orientation to the Fe moments, as confirmed by recent experiments on electron-induced spin-polarized electron emission [39]. The small spin polarization beyond 0.5 ML indicates a loss of in-plane ferromagnetic order and the occurence of antiferromagnetic or ferrimagnetic order. This is in accordance with calculations based on density functional theory [40], showing that (antiparallel) coupling between Mn moments prevails for the full first Mn layer compared to the (antiparallel) Mn–Fe coupling dominant in the submonolayer regime.

4.2. Spin-polarized electron emission

Grazing scattering of keV ions leads to kinetic emission of copious amounts of target electrons from the conduction band with predominantly low energies [41,42]. Under the assumption of spin-conservation during emission process, the spin and, possibly, energy-resolved detection of these electrons yields information on the spin part of the net magnetic moment at the topmost surface layer. Although a general quantitative relationship between electron spin polarization and surface magnetization is not known either, concepts of well-established electron-induced electron spectroscopies can be adopted [43].

Following first experiments on ion-induced spin-resolved electron emission by Kirschner et al. [44], an extension to grazing incidence angles has been proposed by Rau et al. [23,24,45]. Their experiments on surfaces of bulk crystals and ultrathin films showed polarization values comparable to the mean conduction band polarizations, but the (spin-resolved) energy distributions were completely different from those of electron-induced spectra. The latter finding is in contrast to recent studies by Pfandzelter et al. [46,47]. In particular, ion-induced spectra are also dominated by a secondary electron cascade peak with a concomitant enhancement of the spin polarization towards the smallest electron energies. This “spin filter effect” can be explained in terms of spin-dependent electron mean free paths [48]. Thus, energy resolution is mandatory and electrons with energies below about 4 eV have to be discarded from a spin analysis, if a maximum surface sensitivity of the technique is aspired [46,47].

Fig. 6 shows the spin polarization of 4–10 eV electrons emitted by 25 keV protons grazingly

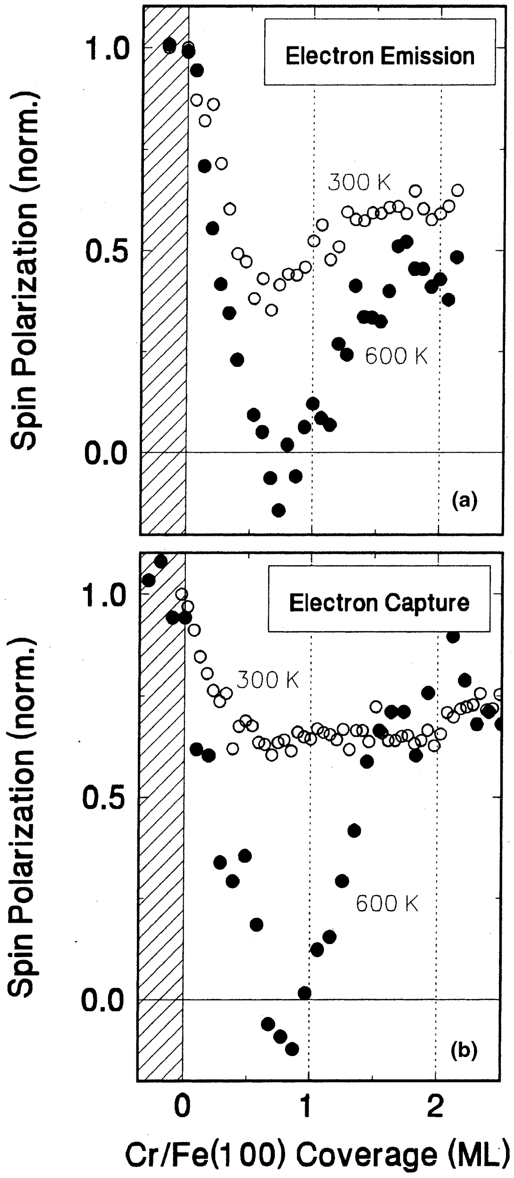

Fig. 6. (a) Spin polarization of low-energy (4–10 eV) secondary electrons excited by grazingly scattered 25 keV H^+ ions during growth of Cr on Fe(1 0 0) at 600 K (solid circles) and 300 K (open circles), respectively. (b) Spin polarization of fluorescence light emitted in the HeI $1s2s\,^3S$–$1s3p\,^3P$ transition after electron capture by grazingly scattered 25 keV He^+ ions.

scattered during growth of Cr on magnetized Fe(1 0 0). For temperatures around 600 K, where growth proceeds in a nearly perfect layer-by-layer mode, we observe a pronounced oscillatory behavior (Fig. 6(a), solid circles). This points to a layer-by-layer oscillation of Cr moments, in accordance with the layered antiferromagnetic order in thicker films [49] and bulk crystals. The polarization minimum around 1 ML coverage is less pronounced at 300 K (open circles). We ascribe this to a rougher growth front, entailing an interaction of the protons with film patches of variable thickness.

A comparison between data obtained by electron *emission* and electron *capture* (Figs. 6(a) and (b), respectively), for the same film–substrate system (Cr/Fe(1 0 0)) shows a close similarity. This demonstrates that these conceptually quite different techniques have similar surface sensitivities and gives further evidence that the experimentally determined spin polarization is a measure for the net magnetic moments at film surfaces.

5. Concluding remarks

We have discussed novel techniques based on grazing scattering of keV light ions to study ultrathin epitaxial films. Depending on the choice of the experimental observable (scattering angle, electron capture, electron emission), information on growth and morphology, elemental composition, and magnetic order can be gained with an extreme sensitivity to the topmost atomic layer of the films.

The techniques hardly face any restrictions concerning growth temperature, deposition rate, or film–substrate combination, but require sufficiently smooth surfaces. This is of minor importance for studies based on electron *capture*, as we could demonstrate by an overlayer experiment using ion beams with varying incidence angles ranging from grazing to normal incidence [50]. Film smoothness is crucial, however, in *kinetic emission* of electrons, since penetration of ions mediated by surface steps gives rise to a contribution to the signal from subsurface layers. This could be suppressed by making use of *potential emission* of electrons, induced by multiply or highly charged ions [51].

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