Electronic interaction of light, keV ions in transition metal nitrides

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Abstract

We investigated the specific electronic energy loss of protons and He ions with keV energies in different transition metal nitrides of technological interest using low- and medium energy ion scattering. Data were obtained from two different time-of-flight setups and show good agreement. For proton stopping in the light nitrides, i.e. TiN, VN and CrN, very similar stopping cross sections per atom were found, which coincide with literature data for N\textsubscript{2} gas for primary energies \(\leq 25\) keV. For chemically rather similar nitrides with metal constituents from the 5\textsuperscript{th} and 6\textsuperscript{th} period, i.e. ZrN and HfN, electronic energy loss was observed to be significantly higher compared to molecular N\textsubscript{2} gas. For He ions, electronic energy loss in all nitrides was found to be significantly higher compared to the equivalent data in N\textsubscript{2} gas. Additionally, deviations from velocity proportionality of the observed electronic energy loss are observed. A comparison with predictions from density functional theory for protons and He ions yields a high apparent efficiency of the energy loss for the latter projectile. These findings are considered to indicate the contributions of additional mechanisms – besides electron hole pair excitations, such as electron capture and loss processes of the projectile.

Keywords: electronic stopping, low and medium energy ion scattering, transition metal nitrides, HfN, ZrN, TiN, VN, CrN
1. Introduction

Ions moving in matter deposit energy due to interaction with either electrons or nuclei of the target, i.e., due to electronic and nuclear stopping. A measure for this energy loss is the stopping cross section (SCS) \( \varepsilon = dE/(n \cdot dx) \), which corresponds to the energy loss \( dE \) per path length \( dx \) with the target atomic density \( n \). Accurate knowledge of electronic stopping is not only necessary for fundamental understanding of electronic interactions in solids, but is also crucial for applications of ion beam analysis (IBA) techniques, e.g., for characterization of thin films, surfaces and nanomaterials [1–5].

For primary energies of at least several hundred keV, energy loss of light ions is mainly due to electronic excitations, i.e., electronic stopping. In this energy regime trajectories are well described within the single scattering model. Towards lower projectile energies, ion-solid interaction gets more complex, i.e., screened Coulomb potentials as well as multiple scattering models are required to properly describe energy loss along the trajectory of the projectile. At these low energies both nuclear and electronic stopping contribute to the stopping power, the latter being dominated by excitation of valence electrons. Consequently, electronic stopping is sensitive to changes in the density of states, as it is the case of compounds. Deviations from Bragg’s rule, i.e., additivity of stopping power in a compound according to stoichiometry, are well documented in literature for energies around and below the stopping maximum, e.g., in oxides [6,7], phosphides [8] and silicides [9].

A simple, yet powerful description of target electrons is in terms of a free electron gas (FEG) [10]. In the low energy regime, this approach results in proportionality of the electronic stopping power to the ion velocity, \( dE/dx = Q(Z_1, n_e) \cdot v \). Here, \( Q \) is equivalent to a friction coefficient, which depends on the atomic number of the ion \( Z_1 \) and the density of the FEG \( n_e \). Usually, the FEG is characterized by the Wigner-Seitz radius, \( r_s = (3/\pi n_e)^{1/3} \) (see e.g., [11]), corresponding to a sphere which contains one electron. Nonlinear density functional calculations yield friction coefficients for different projectiles [12,13]. For slow protons, these DFT calculations are in very good agreement with experiments in manifold target materials by use of effective \( r_s \) values [14]. In a recent study, a breakdown of the FEG model was reported for proton stopping in rare-earth and early transition metals [15]. Even in FEG metals like Al, electronic interactions of helium projectiles are more complex [16–18]. Consequently, for He ions deviations from DFT predictions are reported in literature for many target systems [9,19,20].

Electronic stopping of slow protons has been studied quite intensively, at energies around the stopping power maximum [21,22], as well as at low proton velocities [7]. Scaling of the stopping cross section with the number of O atoms per building block was observed, with values for \( \varepsilon_{O,oxide} \) that exceed the corresponding values in the gas \( \varepsilon_{O_2,gas} \) by a factor of ~ 2. Under the assumption that the electrons are located at the O atoms, the energy loss was attributed to the excitation of the O 2p electrons. For nitrides, below the stopping maximum experimental data are available only for TiN. Here, proton stopping cross
sections per atom in TiN [19] and N₂ gas [23] are similar as well, resulting in a factor of ~ 2 in the stopping per N atom – in accordance to the observations for oxides and LiF. Again, the number of valence electrons per building block in the nitride and in N₂ is similar; TiN is expected to have 7 weakly bound electrons, whereas in N₂ gas there are 3 electrons in a N atom.

To obtain further knowledge on electronic stopping in different nitrides we present data for protons and He⁺ ions in CrN, VN, ZrN, HfN and TiN below the stopping maximum. The group IV and V nitrides are refractory compounds and therefore, also of technological interest [24–26]. However, stopping data are scarce for nitrides with virtually no data for transition metal nitrides. Only limited data are available for He in SiN, GaN and InN around and above the stopping maximum [23], i.e. energies exceeding the values commonly relevant in ion implantation and sputtering. Of these datasets, in particular InN is of interest, due to significant deviations of the data from SRIM predictions below the stopping maximum.

2. Method

Information on the electronic energy loss was deduced from energy spectra of backscattered projectiles. We used two different time-of-flight (ToF) setups to cover a primary energy regime of ~ 1 keV up to ~ 150 keV. In the low energy ion scattering (ToF-LEIS) setup ACOLISSA [27] measurements with protons, deuterium and He ions for primary energies up to 10 keV have been performed at Linz university. This setup features a fixed backscattering angle of θ = 129° with a detector solid angle of 2 × 10⁻⁴ sr. The medium energy regime was covered with the use of a 350 kV Danfysik ion implanter and a subsequent ToF-medium energy ion scattering (MEIS) beam line [28] with a minimum projectile energy of 20 keV and a variable backscattering angle θ in the range from 90° to 160° located at the Tandem Laboratory at the Uppsala University. In the ToF-MEIS setup, both protons and molecular ions were used to obtain an overlap in the stopping data between the two laboratories.

We studied two different types of samples: first, nm thin films sputter-deposited on a light substrate (HOPG), and second, thick high-purity bulk nitrides. For the thin films, carbon was chosen as substrate to allow a better disentanglement of the metal peak and the background especially for spectra with lower primary energies.

VN, CrN, ZrN and HfN thin films with intentional thicknesses of 15 and 30 nm were deposited by reactive DC magnetron sputtering in (Ar/)(N₂) atmosphere. An elemental V, Cr, Zr and Hf target with 90 mm diameter was assembled in a high vacuum laboratory scale six-way reducing cross and the target-to-substrate distance was 10 cm. The carbon substrates were heated to 400 °C and the base pressure after heating/prior to deposition was always < 2×10⁻³ Pa. N₂/(N₂+Ar) gas flow ratios of 100 %, 100 %, 20 % and 30 % were employed for the growth of VN, CrN, ZrN and HfN, respectively. A power of 100 W
was applied to the cathode at 0.5 Pa deposition pressure. The deposition time was adjusted accordingly based on reference synthesis experiments for 60 minutes combined with cross-section scanning electron microscopy thickness measurements. The venting temperature was < 40 °C for all synthesis experiments in order to minimize oxygen incorporation during exposure to atmosphere [29].

The highly crystalline TiN film was sputtered in a cylindrical UHV vacuum chamber (Kurt J. Lesker CMS-18) equipped with a load-lock and evacuated by a cryopump (CTI CryoTorr 8). The base pressure was below 10⁻⁵ Pa. The substrate table was rotated at 20 rpm and kept at floating potential. The pulsed DC power to the target was supplied by an Advanced Energy Pinnacle Plus power supply. Pure nitrogen (30 sccm) was introduced in the chamber and the processing pressure was 0.12 Pa. The substrate temperature was kept at 750 °C and the 4 inch target was fed with 800 W of pulsed DC (resulting in a target current of 1.35 A) with a frequency of 50 kHz and a pulse off-time of 0.5 μs.

The thicker, polycrystalline ZrN, and HfN film layers were grown in an industrial deposition system [30] employing rectangular 8.8×50 cm² elemental targets by reactive dc magnetron sputtering (DCMS) in Ar/N₂ gas mixtures at the total pressure of 3 mTorr (0.4 Pa). The N₂-to-Ar flow ratio was optimized for each target material to obtain stoichiometric single-phase layers. Films were grown on Si(001) substrates sequentially cleaned in acetone and isopropanol and mounted 18 cm away from the target surface. The average target power was 2 kW, while the substrate bias was set at -60 V DC. Two resistive heaters operating during film growth at 8.8 kW each, ensure the substrate temperature of (470±12) °C. All films are exposed to the laboratory atmosphere at very similar venting temperatures 𝑇_v = (230±20) °C in order to avoid significant influence of 𝑇_v on the thickness of formed surface oxide layer [29]. More details related to sample deposition as well as thorough characterization are reported in Ref. [31].

All samples were characterized with the use of Rutherford Backscattering Spectrometry and ToF-Elastic Recoil Detection Analysis (ERDA) at the Tandem Laboratory to evaluate their stoichiometry, purity and areal density. An extensive discussion of the setups and typically employed procedures for data evaluation can be found elsewhere [32]. The thickness measured as areal density was converted into Å via the bulk densities for the nitrides [33]. The resulting thicknesses are in good agreement with physical thickness measurements by scanning transmission electron microscopy, which confirms the density of the films being close to bulk materials. In Tab. I we show an overview of composition as well as thickness of the investigated samples as obtained from RBS & ERDA. All of the thin films exhibit low Z impurities mainly O, but also small amounts of C or Ar from the sputtering process with concentrations for all impurities < 13 %. In Hf and Zr, the respective other metal was found as impurity in all samples (due to their chemical similarity, Hf and Zr are difficult to separate).

In RBS normalization of the charge × solid angle product with respect to simulations using SIMNRA [34] can be performed by either using the intensity of the yield in the plateau originating from the carbon substrate or by a relative measurement of the sample to e.g. Au, Ag or Cu bulk films. In both
cases, the electronic stopping in these materials has to be well-known [35]. However, for C the scatter in published electronic stopping data at ~ 400 keV is larger than for Au at ~ 2 MeV. The different relevant energies result from the large difference in the corresponding kinematic factors for C and Au. For measurements relative to Au or Cu a systematic uncertainty of < 2 % from the electronic SCS has to be considered [36]. For the determination of the nitrogen content a statistical uncertainty of ~ 4 %, due to the background in the RBS spectra originating from impurities in the C-substrate and pile-up in the detector has to be considered.

|     | thickness [Å] | N/TM | impurities [%] | C [%] | O [%] | Ar [%] | Zr / Hf [%] |
|-----|--------------|------|----------------|-------|-------|--------|-------------|
| HfN | 132          | 1.27 | 7              | -     | 2.5   | 2      | 2           |
|     | 262          | 1.38 | 6              | -     | 2     | 1.5    | 2.5         |
| thick [31] | 1.265 |      |                |       |       |        |             |
| ZrN | 133          | 1.20 | 10             | -     | 10    | 0.5\(^1\) | 0.2\(^1\) |
|     | 277          | 1.20 | 5              | -     | 5     | 0.5\(^1\) | 0.2\(^1\) |
| thick [31] | 1.00  |      |                |       |       |        |             |
| CrN | 149          | 1.02 | 8              | 1.8   | 6.2   |        |             |
|     | 300          | 1.08 | 7.1            | 1.8   | 5.3   |        |             |
| VN  | 304          | 1.15 | 12.7           | 4.6   | 8.1   |        |             |
| TiN | 85           | 1.09 | 8              | -     | 8     |        |             |

Tab. I: Sample thicknesses and composition of the investigated transition metal nitrides. All thin films were grown on HOPG. Typically, for nitrides we give the ratio of nitrogen to metal constituents (N/TM).

At the employed low- and medium- primary energies, a comparison of the spectra of backscattered projectiles to Monte-Carlo simulations is necessary to disentangle electronic stopping from effects of multiple scattering and nuclear stopping. For this purpose, we used the TRIM for backscattering code (TRBS), which allows adjustments in the interatomic potential, affecting contributions from multiple scattering, and for electronic stopping along the trajectories. In order to evaluate electronic stopping from the measured energy spectra, \( \varepsilon \) was varied in the simulation to obtain optimum agreement between the relevant features in experiment and simulation. Note, that this procedure yields a mean stopping cross section that is averaged over all (possibly impact parameter dependent) electronic energy loss processes in the target.

In the TRBS simulations, we employ the Ziegler-Biersack-Littmark (ZBL) potential [37], which in general shows good agreement between the experimental spectra and the TRBS simulation. However, for HfN deviations in the multiple scattering background are observed for \( E_0 \leq 100 \) keV. At lower primary energies screening length corrections are needed to reproduce the background in the experiment. A recent study investigates the influence of uncertainties in the scattering potential on the evaluation of

\(^1\) not considered for the evaluation of \( \varepsilon \)
electronic energy loss. As a result, the evaluation of the peak width for energies $E_0 \leq 100$ keV may require differences in electronic stopping, necessary to obtain a good fit, up to $\sim 3\%$ depending on the employed potential – ZBL or Thomas-Fermi-Moliere – and a possible screening correction [38].

For thin films, electronic stopping can be deduced from the width of the metal peak, if film composition and thickness are known. Figure 1 shows typical time-of-flight spectra converted to energy obtained with the (a) ToF-LEIS and (b) ToF-MEIS setup. Panel (a) depicts the spectrum for 8 keV protons scattered from a TiN film with a nominal thickness of 85 Å on a carbon substrate; in panel (b) the spectrum for 60 keV He$^+$ ions backscattered from a 149 Å thin CrN film on carbon is plotted for a scattering angle of $\theta = 155^\circ \pm 2^\circ$. TRBS simulations with a best fit to the experiment as well as modifications of $\varepsilon$ by $\pm 10\%$ and $\pm 5\%$ are presented as red solid and dashed lines, respectively. Note, that the stopping deduced from the simulation corresponds to all electronic losses experienced in the film including impurities. We therefore, performed a correction according to Bragg’s rule [39] to obtain the electronic SCS in the nitride, as described in Ref. [40]. This correction in the SCS amounts to at most 6%, with largest impact on the low energy data.

![Fig. 1: ToF converted energy spectra for (a) 8 keV H$^+$ scattered from TiN and (b) 60 keV He$^+$ ions scattered from CrN. The experimental data (black squares) are compared to TRBS simulations with different electronic stopping values: a best fit and simulations with variations in the electronic stopping of (a) $\pm 10\%$ and (b) $\pm 5\%$ are depicted as red solid and dashed line, respectively.](image-url)
spectrum [41]. In this way, the influence of possible surface impurities is excluded. Note, here the electronic stopping in the reference material \( \varepsilon_{\text{ref}} \) must be known in order to obtain SCS data for the sample of interest \( \varepsilon_x \). Consequently, uncertainties in \( \varepsilon_{\text{ref}} \) yield a systematic error in the evaluated \( \varepsilon_x \). In general, for these measurements a reference with similar atomic number as the sample of interest is chosen in order to minimize the influence of uncertainties in the scattering potential on data evaluation. Therefore, Au [42] and Ag [43] have been used as reference for HfN and ZrN, respectively.

3. Results and discussion

The electronic stopping data of protons in five different nitrides are plotted in Fig. 2: HfN (green diamonds), ZrN (red points), TiN (black squares), VN (dark blue pentagons) and CrN (magenta hexagons). Where recorded (HfN, ZrN), data obtained from both evaluation methods and both setups agree within their experimental uncertainties. Additionally, SCS data from literature for TiN in the medium energy regime [19] as well as for \( \text{N}_2 \) gas [23] are plotted as grey triangles and blue asterisks, respectively. For TiN our low energy data agree very well with literature. Due to the lack of data for the other nitrides we compare our results at first hand to predictions by Bragg’s rule [39] using SRIM-13 [44] data shown as dashed lines with the same color code as the experimental data. The predictions do not quantitatively describe stopping in this energy regime, with deviations up to \(~ 22\% \) observed. Predictions based on SRIM reproduce, however, the correct order of the magnitude of the experimental data: ZrN exhibits highest and CrN and VN lowest stopping cross sections. Based on the principles of SRIM these observations can be understood since for some metals, as e.g. Hf and Zr, either no or only scarce experimental data are available, especially below the stopping maximum [23]. In these cases, SRIM stopping is based on interpolations from other metals. For samples of different stoichiometry for the same compound, as e.g. HfN, only one prediction by Bragg’s rule is depicted in Fig. 2, since the small difference in the SCS resulting from different stoichiometries could not be resolved within experimental uncertainties.

For all proton stopping data below \(~ 1\) a.u., \( \varepsilon \) exhibits velocity proportionality as predicted for a FEG [10], with different slopes for different nitrides. For velocities up to \(~ 1.0\) a.u., the \( \varepsilon/\text{atom} \) values for TiN, VN and CrN coincide with \( \varepsilon/\text{atom} \) in \( \text{N}_2 \) gas within experimental uncertainties. This observation means that in the nitrides the SCS per building block is as high as it is per \( \text{N}_2 \) molecule in the gas, or in other words, the nitride SCS per N atom is twice as high as it is in the gas phase. This behavior is in striking analogy to the oxides, for which the SCS/O atom is found twice as high as for \( \text{O}_2 \) gas [7].
Fig. 2: Electronic stopping cross sections for protons in HfN (green diamonds), ZrN (red points), TiN (black squares), VN (dark blue pentagons) and CrN (magenta hexagons). Additionally, data from literature are plotted for TiN [19] and N₂ (gas) [23]. The different dashed lines correspond to Bragg’s rule predictions with SRIM-13 data in the color code of the corresponding materials. A fit to the CrN SCS data is depicted as magenta solid line resulting in an effective density of the FEG of \( r_{\text{eff}} = 1.62 \) according to DFT calculations [45].

In the following section, we will discuss the observed effects from two distinct perspectives, i.e. an atomistic one, as well as employing a free electron gas model. From the observed similarity to what has been observed for oxides, the present data for protons could be naïvely understood in an atomistic picture with complete electron transfer. If the bonds in the nitrides were ionic, one could assume that three valence electrons of the metal atoms would be transferred to N atoms and N 2p⁶ would be twice as efficient in electronic stopping as N 2p³, ignoring changes in binding energy and their impact on excitation. Note, in this context, that also for strongly ionic compounds like Alkali halides, where valence electrons are clearly located at the anions [46], a comparison of the stopping cross sections of the compounds to the corresponding data for the anions in the gas phase results in similar observations. For LiF [47,48], \( \varepsilon / \text{atom} \) for protons was observed to be similar to experimental data for Ne [49] and to expectations for F [50]. Equivalently, comparison of \( \varepsilon_{\text{LiF}} / \text{F} \) atom LiF to \( \varepsilon_{\text{Ne}} \) and the prediction for \( \varepsilon_{\text{F},\text{gas}} \) yields \( \varepsilon_{\text{LiF}} / \text{F} \) atom \( \approx 2 \varepsilon_{\text{Ne}} \approx 2 \varepsilon_{\text{F},\text{gas}} \) for 10 keV protons. There are, however, major differences in the electronic structures of fluorides, oxides and nitrides: While in the oxides the density of valence
electrons is dominantly centered at oxygen, in the nitrides the valence electron densities are comparable at the metal sites and at N. For the oxides studied in [7], no significant evidence for an influence of the different band gaps (0 to 10 eV) was observed. Thus, we expect the observed simple scaling to be the result of a complex interplay of modifications of the electronic structure when comparing the more ionic, anion-centered electronic structure to a more covalent bond as in the nitrides together with drastically changing ionization energies.

A completely different approach is to compare the present data to predictions for a FEG as obtained from DFT. In such an approach, a fit to the CrN data yields a friction coefficient of $Q_H = 0.294$ a.u. resulting in an effective electron gas density of $r_{s,\text{eff}} = 1.62$ according to DFT calculations [45]. This density would correspond to ~7 electrons contributing to electronic stopping for CrN as well as VN and TiN, due to their similar SCS, in reasonably good agreement with expectations from plasmon frequencies [51–53]. However, we are well aware that the unperturbed density of states for the investigated compounds is fundamentally different in structure from a FEG, with occupied and unoccupied electronic states featuring high densities in narrow energy bands. Also, the comparable velocities of projectiles and electrons involved in the excitation process may require a more complex dynamic description. For example, in a recent work, the free electron gas model has been shown to break down for early transition metals from the 6th period [15]. At the same time, the magnitude of the electronic energy loss of slow ions in ionic crystals such as LiF could be successfully reproduced in this framework [54].

For the systems with most complex electronic structure, however, i.e. ZrN and HfN, the SCS is significantly higher than for TiN, VN and CrN, with highest SCS for ZrN. This observation cannot be explained in any of the two perspectives above considering binding type the electronic structure in valence and conduction band. The real nature of excitation is thus considered to depend on details of electronic structure, its expected dynamic nature in the interaction and associated effects on excitation, which require more detailed modelling.

In Fig. 3 the SCS data for He ions are presented with green diamonds for HfN, red circles for ZrN, dark blue pentagons for VN and magenta hexagons for CrN. Data from literature are plotted for TiN (grey triangles) [19] and N$_2$ gas (blue asterisks) [23]. We again show SRIM predictions according to Bragg’s rule, due to the lack of existing experimental data for the other compounds. Similarly as for protons the order of the predicted values is the same as we observe with our experimental data, however, with significant discrepancies in the absolute values.
Fig. 3: Stopping cross section of helium ions in HfN (green diamonds), ZrN (red points), VN (dark blue pentagons) and CrN (magenta hexagons). Data from literature are plotted for TiN (grey triangles) [19] and N\textsubscript{2} gas (blue asterisk) [23]. The different dashed lines correspond to electronic stopping predicted from SRIM according to Bragg’s rule. The magenta line would correspond to the electronic energy loss as predicted from DFT assuming the same density for the FEG as obtained for protons.

In contrast to protons, in all nitrides, the SCS/atom for He ions is significantly higher than in N\textsubscript{2}, by up to a factor of two for low energies, in clear contrast to expectations from a naïve atomistic model. Again we can also compare the results to predictions by the FEG-model. The magenta line corresponds to electronic stopping as predicted from DFT with the electron density as obtained for protons ($r_{\text{eff}} = 1.62$). It can be clearly seen, that also DFT based on the same interaction mechanisms and electron gas density as employed to model our data for protons underestimates the energy loss of He ions. Beyond what has been said for protons, this can be taken as an indication for a strong contribution of an energy loss process that is active in addition to electron hole pair excitation, i.e. electron capture or loss processes between projectile and target affecting the effective charge state for He projectiles. A similar discrepancy between data for protons and He has been observed for other target materials with vastly different electronic structures [17,55,56].

In a more detailed analysis of the velocity dependence, data for TiN, VN and CrN show an apparent threshold when extrapolating medium energy data for He stopping towards zero velocity. In ZrN and
HfN, $\varepsilon_{\text{He}}$ is proportional to the ion velocity for 0.2 a.u. < $v$ < 1 a.u. However, at velocities below ~ 0.2 a.u. it deviates from this proportionality and extrapolation towards $v \to 0$ leads to a positive offset. While such an offset value is per se meaningless; it is, however, well in agreement with the presence of an additional energy loss process, with a different and weak velocity dependence.

4. Summary
We presented electronic stopping data for H and He ions in different transition metal nitrides at energies below the stopping maximum. Samples were synthesized following different routines, and with different physical structure i.e. significantly different thickness. Together with extensive characterization this procedure was conducted to minimize a possible influence of sample impurities and microstructure. Stopping cross sections were obtained from evaluating width of resulting energy spectra. For thicker films, stopping cross sections were deduced from fitting the spectral intensity. In this case electronic stopping was evaluated relative to a reference material of accurately know stopping power, i.e. Ag and Au. Where both methods have been applied, good agreement of the deduced datasets was observed.

For protons electronic energy loss below ~ 1 a.u. (25 keV) in the light transition metal nitrides, i.e. TiN, VN and CrN, was found to be a factor of ~ 2 more effective than in molecular N$_2$ gas, similar to observations for oxides [7]. However, for ZrN and HfN electronic energy loss is significantly higher. For He ions, $\varepsilon$ in the nitrides is more effective than expected exclusively from electron-hole pair excitations. The observed deviations from velocity proportionality of the electronic stopping for He ions indicate an additional contribution to the energy loss, such as electron capture and loss processes between projectile and target, which alter effective charge states. The obtained data are considered to provide reference material for advanced time-dependent modelling of ion-matter interaction, which can adequately describe such phenomena to confirm or reject this hypothesis. At the same time, data are expected to contribute to more reliable semi-empirical modelling of the energy loss and accurate depth and range profiles in applications.

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