Photon emission spectroscopy of NiAl(110) in the scanning tunneling microscope

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Spectroscopic measurements have been carried out of the light emitted from the NiAl(110)/W tunnel junction of a scanning tunneling microscope. The data reveal two prominent emission lines in the visible and near-infrared region. Corresponding model calculations assign the observed light emission to the radiating decay of the tip-induced plasmon excited in the tip-sample cavity. In agreement with the theory, a low- and a high-energy mode of the plasmon can be distinguished in the experimental data. Since the excitation probability of the two modes is determined by the size of the tunnel cavity, it can be influenced by the radius of the tunnel tip. A blunted tip favors the observation conditions of the higher mode.

The first observation of light emission from the tunnel junction of a scanning tunneling microscope dates back more than ten years.[1] Nevertheless, the underlying mechanisms are still of great experimental and theoretical interest.[2] This results mostly from the unique possibility of detecting the characteristics of the photon emission with the highest spatial resolution and determining optical and dielectric properties on a nanometer scale. Two main mechanisms responsible for the observed light emission have been identified so far.

(i) In the first case, the tunnel tip serves as a local electron emitter injecting hot electrons or holes into the sample surface. The subsequent recombination process to states near the Fermi level can occur via optical deexcitation, leading to the emission of photons. Especially for materials with a band gap, the mechanism is very efficient. The technique was therefore widely used to investigate the optical and electronic properties of semiconductors with direct[3–5] and indirect band gaps.[6,7]

(ii) In the second case, the strong electromagnetic coupling between the tip and the sample is responsible for the photon-emission process. Collective electronic oscillations, so-called tip-induced plasmons (TIP's), driven by the inelastic part of the tunnel current are excited in the coupled electron gases of tip and sample.[8] The decay of these interface plasmons gives rise to the observed enhanced light emission.[9] For materials with low absorption coefficients, especially noble metals, unexpectedly high quantum efficiencies have been measured.[10,11] Characteristic light emission spectra are governed by a single emission line corresponding to the first mode of the TIP. Also higher modes of the plasmon oscillation, characterized by nodes of the electromagnetic field inside the tunnel cavity, are obtained by theory, and have been identified experimentally in the case of an Ag/Ag tunnel junction.[12] Although the importance of TIP's for the photon emission from transition metals is still an open question, only a few scanning tunneling microscopy (STM) studies have been reported on this field, revealing a faint, unstructured light emission.[13,14] The strong damping of the interface plasmon oscillations due to the influence of the metal *d* electrons makes the observation and spectral resolution of the emitted photons more difficult. In addition, alloys characterized by complex dielectric and optical properties are interesting candidates for checks of the validity of the theory of TIP's. For alloys, no investigations of this kind have yet been reported to our knowledge.

In the present work, we have combined these two aspects, choosing a Ni(50%) Al(50%) single crystal for photon-emission spectroscopy in the STM. The alloy shows a complex dielectric function as a result of the interplay between the Al *s*,*p* electrons and Ni *d* electrons.[15] The electronic states near the Fermi level have mainly *d* character.[16] In this paper, we present light emission spectra obtained from NiAl(110) with an STM. From the comparison with calculated spectra, we conclude that for this alloy the decay of TIP's is the dominating mechanism for the observed light emission.

The experiments have been performed in two ultrahigh-vacuum (UHV) chambers connected by a UHV-transfer rod facility for *in situ* sample preparation and STM analysis (pressure $p<5\times10^{-10}$ mbar). To maximize the acceptance angle for the photon detection, a beetle-type STM with its open construction has been used.[17] The STM is completely surrounded by a parabolic mirror, whereby the tip-sample region is adjusted in the focal point. Outside the vacuum chamber, the light is focused on the entrance slit of a grating spectrograph and detected with a liquid-nitrogen cooled CCD camera. A wavelength range for photon detection between 200 and 1200 nm (approximately 1–6 eV) is accessible to the experiment, restricted by the performance of the CCD chip. The preparation chamber is equipped with standard UHV facilities for sample preparation and analysis, including an ion gun and a low-energy electron-diffraction (LEED) system. The tunnel tips were electrochemically etched from a polycrystalline tungsten wire. A NiAl single crystal cut perpendicular to the [110] direction served as a sample. The cleaning procedure of the surface followed a standard recipe of alternating cycles of Ar sputtering and annealing to 1100 K, previously described in Ref. 18. For all photon-emission spectra of the NiAl(110) surface, a light

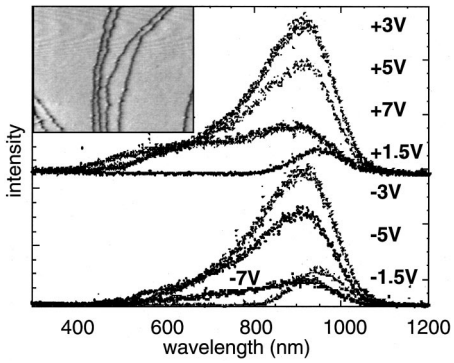

FIG. 1. Experimental photon-emission spectra for the NiAl(110)/W tunnel junction for both polarities. The tunnel current was set to 5 nA; the tunnel bias refers to the tip. The inset shows an STM image of the NiAl(110) surface (image size, 130×130 nm; tip voltage -2 V; tunnel current, 0.5 nA).

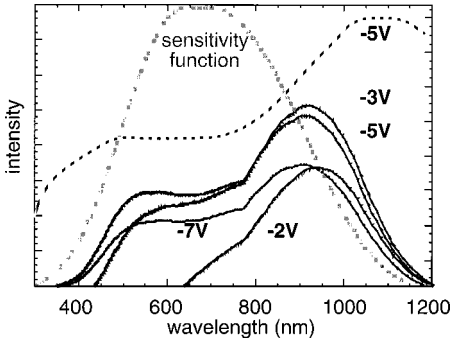

FIG. 2. Calculated photon-emission spectra for the NiAl(110)/W tunnel junction, uncorrected (broken line) and multiplied with the sensitivity function of the optical system (solid lines). The tunnel voltage is given relative to the tip. A tip radius of 50 nm and a tunnel current of 5 nA were used in the calculation. The sensitivity function of the optical system is also shown in the figure.

accumulation time of the CCD camera of 500 s per spectrum and a tunnel current of 5 nA were used. An STM image of the examined sample region was taken before and after each spectroscopic run to exclude morphological changes of the surface. To circumvent possible effects of the surface topography, the spectra were measured on atomically flat terraces with a distance to the adjacent step edges of more than 20 nm (inset of Fig. 1). The spectra represent raw data and have not been corrected for the sensitivity function of the optical system. For a comparison of measured and calculated spectra, this sensitivity will be taken into account later. Values for the bias voltage are always referring to the tip.

Figure 1 shows a series of photon-emission spectra measured at different tunnel voltages and polarities. The shape of the curves reveals no significant dependence on the direction of the tunnel current. The dominating feature in all spectra is a broad emission line centered at approximately 930 nm. The peak positions remain essentially constant in the voltage range investigated. The onset voltage for photon emission is approximately 1.2 V. In the first spectrum, taken at a tunnel voltage of 1.5 V (1.5 eV corresponds to 823 nm), the complete development of the emission is still suppressed and a considerable redshift of the peak position is noticeable. The line shape of all curves is clearly asymmetrical with a prominent shoulder appearing on the short-wavelength side as the tunnel voltage increases. For ±7 V the shoulder has developed into a second emission line at around 500 nm. The integral emission intensity passes a pronounced maximum at 3–4 V as a function of the applied voltage. As expected, the integral intensity varies linearly with the tunnel current (not shown).

To get a deeper insight into the physical origin of the observed photon-emission behavior, model calculations have been carried out. Since the shape of the spectra does not depend on the polarity of the applied tunnel voltage, the theory which interprets the light emission as the radiating decay of TIP's appeared as an appropriate starting point for the calculation. A detailed description of the theoretical approach can be found elsewhere.[19] In brief, the electromagnetic response of the tip-sample system is calculated in the nonretarded limit by considering a model geometry consisting of a spherical tip in close proximity to a semi-infinite metal sample. The optical properties of the tip and sample materials enter the calculation through experimentally measured dielectric functions. The model gives the electromagnetic response function of the tip-sample cavity and allows the determination of the spectral properties and the intensity of the emitted light. The tip-sample distance corresponding to a given bias voltage and tunnel current and the inelastic transition matrix elements associated with the light emission are calculated in a one-dimensional free-electron model for the tip and sample materials. Calculated results for a set of parameters [tip radius 50 nm, tunnel current 5 nA, work functions $\phi_W=4.5$ eV,[20] $\phi_{\mathrm{NiAl}(110)}=5.1$ eV, (Ref. 21)] modeling the NiAl/W tunnel junction are shown in Fig. 2. Only data for negative tip voltages are presented. The calculated behavior at opposite polarity is very similar due to the nature of the interface plasmon resonance in agreement with the experiment. To make theoretical and experimental results comparable, the calculated spectra have been multiplied with the sensitivity function of the optical system used (solid lines in Fig. 2). An uncorrected curve has been added to Fig. 2 (broken line). The quantum efficiency of the CCD camera vanishes at 1200 nm, thus causing a cutoff of the main emission line calculated at 1100 nm. This leads to a pronounced but artificial blueshift of its peak position. This most prominent spectral feature has to be interpreted as the resonance position of the TIP in the NiAl/W cavity. Its energy position is mainly determined by the dielectric function of the NiAl crystal whose real part exhibits a strong increase to zero combined with a minimum of its imaginary part in the same energy range.[16] The dielectric function of the W tip is comparatively structureless and flat. The strong variation in the dielectric function of the alloy is also responsible for the pinning of the resonance position of the interface plasmon irrespective of the applied tunnel voltage.[22] The small peak in the theoretical spectra at approximately 500 nm can be understood as the second mode of the interface plasmon. This higher mode is comparable to the quadrupole resonance in the Mie theory for the special case of the tip-sample geometry.[23] In contrast to the first resonance, the distribution of the appropriate electromagnetic field is considerably spread out in the tip-sample cavity. The variation of the photon-emission intensity as a function of the applied bias voltage is governed by two competing processes. An increase in the tunnel voltage opens successively new channels

for inelastic tunneling processes and enhances therefore the probability for plasmon excitation. On the other hand, an increasing tunnel voltage at constant tunnel current leads to a retraction of the tip and to a reduced electromagnetic coupling between tip and sample. The calculated integral light intensity for the NiAl/W tunnel junction has a maximum at approximately 3 V.

The peak associated with the first TIP mode can clearly be identified in the experimental data shown in Fig. 1. The observed peak position at 930 nm results from an interplay between the emission characteristics of the interface plasmon and the efficiency function of the optical system and is in good agreement with the theoretical value. Moreover, the calculated intensity variation as a function of the bias voltage is reproduced in the experiment. The total quantum efficiency calculated for a tip bias of 3 V and a tunnel current of 5 nA is approximately 1.2×10^{-6} photons per electron. The corresponding experimental result of approximately 5×10^{-7} photons per electron is considerably lower. The difficulties in the estimation of crucial parameters in the theory of the interface plasmons such as radius or shape of the tunnel tip may be responsible for the discrepancies. The experimental quantum efficiency is, however, similar to the values found for other transition metals (Ti,Fe).[13] More apparently in the experimental spectra is the absence of the peak corresponding to the higher plasmon mode. It is probably masked by the short-wavelength shoulder of the main oscillation and is discernible only at elevated tunnel voltages (over ±7 V). To test the predictions of the theory, we have tried to improve the observation conditions for the higher mode. For this purpose we have used the fact that an enlargement of the tunnel cavity, for instance due to an increase of the tip radius, shifts the excitation probability from the first to the second mode. This is the consequence of a broader excitation width of the higher TIP mode, which can be more easily fulfilled in a complex tip-sample geometry. Also an elevated tunnel voltage, providing more electrons with the required energy for the inelastic tunneling process, favors the excitation of the high-energy mode. Figure 3 shows two spectra measured with an intentionally blunted tunnel tip on a NiAl(110) surface, which has been produced by a controlled collision with the sample.[24] The emission peak at 500 nm due to the second resonance of the TIP is now clearly visible, confirming the predictions of the theory.

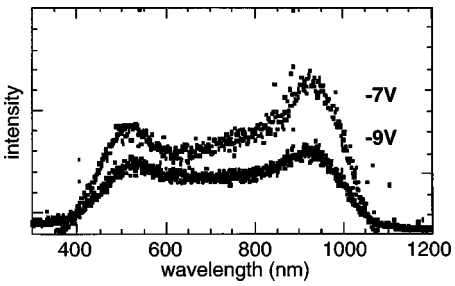

FIG. 3. Experimental photon-emission spectra for the NiAl(110)/W tunnel junction. An intentionally blunted W tip has been used. The tunnel current was set to 8 nA; the bias refers to the tip.

In conclusion, we have obtained photon-emission spectroscopic results on a NiAl(110) surface in an STM. In analogy to noble metals, the decay of TIP excitations is the dominant source of the observed light emission. Conclusively, the excitation of this interface plasmon is not restricted to a high density of free-electron states near the Fermi level of the tip and sample materials. It can also occur for solids characterized by a high *d*-electron contribution to the density of states close to E_F, as verified for NiAl in the present work. However, the influence of the relatively localized *d* electrons leads to a decrease of the emitted light intensity by a factor of 50, compared with results for the Ag/Ag tunnel junction.[10] The experimental spectra reveal two prominent emission lines, which can be attributed to the low- and the high-energy mode of the interface plasmon. The intensity ratio between the two modes can be influenced by changing the radius of the tunnel tip. Optical transitions inside the NiAl crystal, such as interband transitions, could not be identified as a source for the observed emission.

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[9] One can also view the light emission as a one-step process (the model calculation takes this point of view). In this picture the TIP resonance leads to a strong enhancement of the electromagnetic vacuum fluctuations, and hence the increased rate of spontaneous photon emission in the cavity between tip and sample.

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