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Spin-resolved density of states at the surface of NiMnSb

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Spin-resolved photoemission measurements from polycrystalline NiMnSb films reveal spin-resolved density of states which are in qualitative agreement with local spin density functional band structure calculations [Phys. Rev. B **51**, 10 436 (1995)]. The polarization of electrons close to the Fermi level is however found to be at most 40%, in contrast to the predicted half-metallic behavior. This discrepancy is attributed to lower remnant magnetization of the surface region and/or the presence of other phases.

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The discovery of large room temperature spin dependence of the tunneling current[1] in ferromagnet/insulator/ferromagnet structures has generated much interest in these properties due to their possible application as magnetic random access memory (MRAM) elements.[2] One very active area of this research has been the search for ferromagnetic materials with high spin polarization of conduction electrons, in particular the ones with 100% spin polarization, usually referred to as half-metallic ferromagnets (HMF), which would lead to large magnetoresistance (MR) and efficient MRAM devices. Although it was recently shown that HMF properties exist in the low temperature state of the $La_{0.7}Sr_{0.3}MnO_3$,[3] there is a continuing search for room temperature HMF materials that could be used in real devices. One class of materials which have been predicted to exhibit HMF behavior are some Heusler alloys, like NiMnSb.[4,5] However, most of the magnetotransport work employing NiMnSb up to now have reported rather meager MR effects of up to 7%.[6] Since the tunneling is believed to be very sensitive to the spin polarization of conduction electrons near the ferromagnet/insulator interface,[7] from their MR results it is not clear whether NiMnSb does not exhibit HMF behavior or only the surface region is non-HMF. Recent measurements of several materials predicted to be HMF employing Andreev-reflection[8] have on the other hand indicated a large degree of conduction electron spin polarization in several materials, including NiMnSb.

Spin-resolved photoemission technique (SRPES) is an ideal tool for addressing these issues, not only because it is able to directly measure the spin polarization of the electrons close to the Fermi level but also because it is surface sensitive, thus probing the most relevant region of the sample. Earlier photoemission work of Bona *et al.*[9] has found the spin-polarization of photoemitted electrons from *in situ* cleaved NiMnSb crystal to be 50% in the applied magnetic field of 10 kOe. However, these measurements were performed with electrons of very low kinetic energies (threshold photoexcitation), thus the degree of polarization may have been affected by the spin-filtering effects which are known to be significant at these low energies.[10] In this paper we report on energy-resolved SRPES measurements on NiMnSb films at higher photon energies. Although the measured spectra show qualitative agreement with the calculated spin-resolved density of states, the observed spin polarization is only 20–40 % within 0.5 eV from the Fermi level. The binding energy dependence of spin polarization are however consistent with the presence of a component exhibiting half-metallic ferromagnetic behavior as predicted by calculations but with low remnant surface magnetization and/or mixed with another non-HMF phase.

The polycrystalline NiMnSb films were grown on Si substrates in ways described earlier.[11] The substrate temperature was held at 415 °C and no postannealing was performed. The films were 600 Å thick and were capped with 30 Å of Al before they were transferred in air to the SRPES chamber. The spin resolved photoemission measurements were performed at National Synchrotron Light Source (NSLS) using the undulator based SGM (u5u) beam line and an angle- and spin-resolving electron spectrometer.[12] The total electron energy resolution (photon plus electron) in the valence band measurements was 100 meV. The photon incidence direction was set at 45° and photoemission along the surface normal was measured. The films were in-plane magnetized, perpendicular to the photoemission plane. They were sputtered with a differentially pumped ion gun using Ne^+ ions at 1.0 keV, 25 mA emission current and 45° incidence and then annealed with an e-beam heater. The sample temperature was monitored by a thermocouple attached to the Mo plate on which the sample was mounted. The base pressure of the vacuum chamber was $<2\times10^{-10}$ Torr.

The magnetic state of the films was probed with the magneto-optical Kerr effect (MOKE) technique. The magnetic hysteresis curves were square with a coercivity of $\sim$20 Oe and high remnant magnetization ($\sim$95%) at room temperature for films magnetized in plane. No changes in hysteresis curves was observed after cycles of sputtering and annealing. This indicates that the remnant magnetic state is

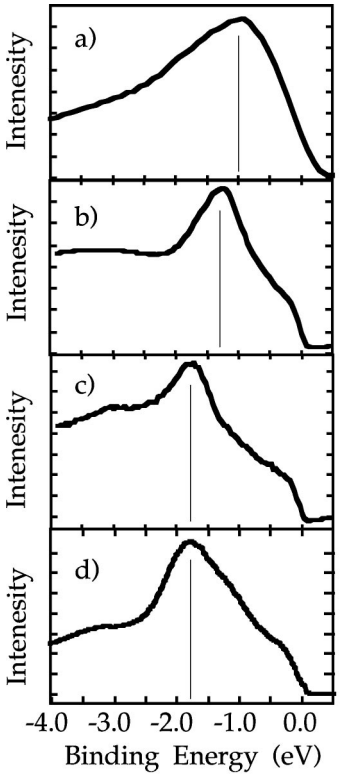

FIG. 1. Spin integrated photoemission spectra from NiMnSb film: (a) after sputtering, (b) after annealing to 320 °C, (c) after annealing to 400 °C, and (d) from cleaved NiMnSb crystal from Ref. 13.

preserved which is important in the spin-resolved photoemission experiments since no magnetic field is applied during the measurement.

First we discuss the sample surface preparation. The surface stoichiometry was monitored with core-level photoemission using the Ni $3p$, Mn $3p$, Sb $4d$, and Al $2p$ peaks and 160 eV photons, while the electronic structure was probed with valence band photoemission and photon energy of 38 eV. The core-level photoemission spectra, at first, showed only the Al $2p$-oxide signal consistent with the presence of Al oxide cap above the NiMnSb films. After sputtering the Al $2p$-metal photoemission peak appeared indicating that 30 Å of Al cap layer was sufficiently thick not to allow the oxidation of the NiMnSb film during sample transfer in air. Further sputtering removed all of the Al, leaving only Ni, Mn and Sb. In general we find that the sputtering cycles preferentially removed Sb and to a lesser extent Mn, leaving Ni enriched films. The sputtering was followed by annealing, which was performed in increasing temperature steps. No appreciable change in the Ni:Mn:Sb ratio was observed up to 200 °C. Above that temperature we observe increase in Sb and Mn (to a lesser extent) concentration, offering a way of restoring the NiMnSb stoichiometry.

The stoichiometry ratio determined from the peak heights of the core-level photoemission spectrum depends on several experimental factors and values of photoelectron cross sections; thus we used them primarily to monitor the relative changes during the sputtering and annealing cycles. We relied instead on the valence band spectra to identify different phases during the surface preparation. A clear correspondence between the changes in NiMnSb stoichiometry (from core-level PES) and the valence band spectra was observed. Figure 1(a) shows a typical valence band spectrum obtained after sputtering cycles. A broad, featureless spectral distribution peaked at ~1.0 eV is suggestive of mixture of metallic-like Ni and Mn components. Sample annealing above 200°C tends to move the valence band maximum to slightly higher binding energies but with relatively little change in the overall line shape. Annealing to 320 °C for 15 min, however, does produce another spectral line shape, which peaks at about 1.2 eV binding energy, and a shoulder at lower binding energies as evident from Fig. 1(b). Annealing to 400 °C produces another distinct change with the valence band maximum now moved to 1.7 eV, the development of a pronounced low energy shoulder and distinct high binding energy peak at 3 eV. Further annealing at even higher temperature produced no changes in the spectral line shape below 4 eV, but gives rise to Si and O segregation from the

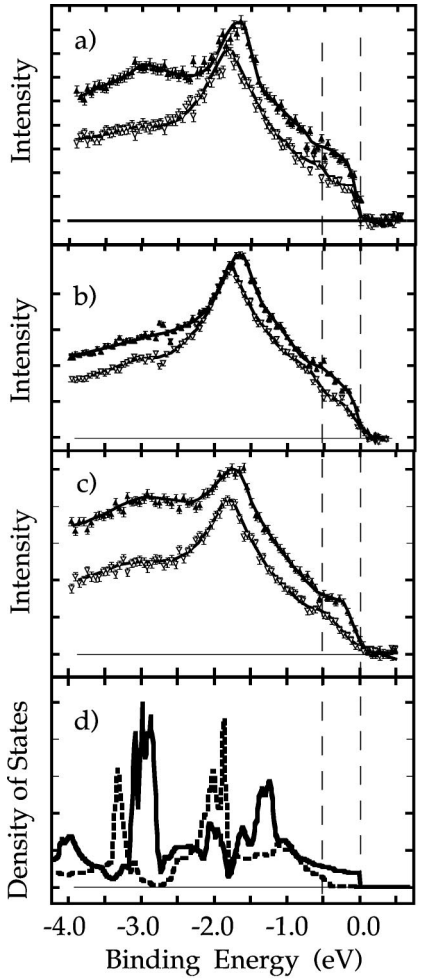

FIG. 2. Spin-majority (▲) and spin-minority (▽) photoemission spectra from NiMnSb annealed to 400 °C at different photon energies: (a) $h\nu = 38$ eV (off-resonance); (b) on Mn-M_{23} antiresonance ($h\nu = 52$ eV); (c) at the Ni-M_{23} resonance ($h\nu = 76$ eV). (d) Calculated spin-resolved density of states from Ref. 15 (full line: majority spin; dashed line: minority spin).

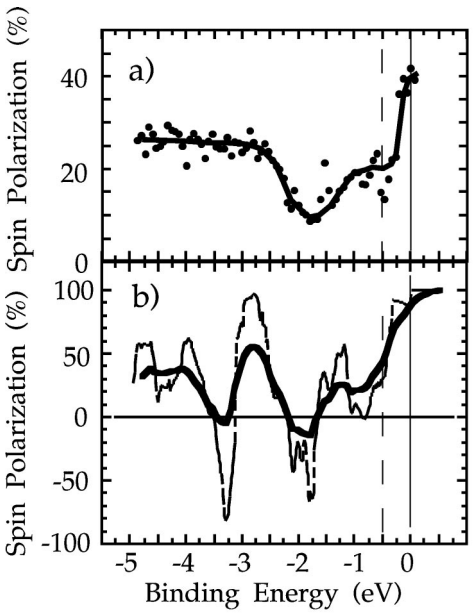

FIG. 3. (a) Electron spin-polarization of spectrum shown in Fig. 2(c). (b) Spin-polarization of the calculated density of states (from Ref. 15) (dashed line: raw data; full line: broadened by photoemission instrumental resolution).

substrate. As seen in the Fig. 1, we observe three distinct valence band line shapes, after sputtering [Fig. 1(a)], after annealing to 320 °C [Fig. 1(b)], and after annealing to 400 °C [Fig. 1(c)]. Comparison of these spectra with spectrum reported by Kang *et al.*[13] from *in situ* cleaved NiMnSb bulk samples [presented for a comparison in Fig. 1(d)] shows clear similarity with our spectrum of Fig. 1(c) in all major features. This we take as an indication that we have regenerated the NiMnSb phase after sputtering off the cap material. It is interesting to note that a similar substrate temperature was used during the film growth (415 °C). We also note that our spectrum in Fig. 1(b) is very similar to the Ni_2MnSb spectra reported by Robey *et al.*[14] Valence band photoemission measurements of NiMnSb film surface taken at different photon energies (30–140 eV) show relatively weak Mn $3p \rightarrow 3d^*$ and Ni $3p \rightarrow 3d^*$ resonances. No change in line shape was observed away from the two resonances indicating no final state effects.

We now turn to the spin-resolved photoemission (SRPES) measurements performed on the surface of the NiMnSb films. Figures 2(a)–2(c) shows the spin-resolved NiMnSb valence band photoemission spectra recorded at different photon energies. For comparison we also show the calculated spin-resolved density of states (SRDOS) of Youn and Min who performed total energy local spin density functional LMTO band structure calculation.[15] All three SRPES spectra [Figs. 2(a)–2(c)] show the majority-spin spectrum with higher overall cross-section than the minority one, simply indicating that the surface of the NiMnSb film is ferromagnetic. There are several differences between the majority-spin and the minority-spin spectral line shape. The spectra recorded with 38 eV photons [Fig. 2(a)] show the minority-spin maximum at somewhat higher binding energy than the majority peak (by ~ 0.15 eV), indicating that the two peaks

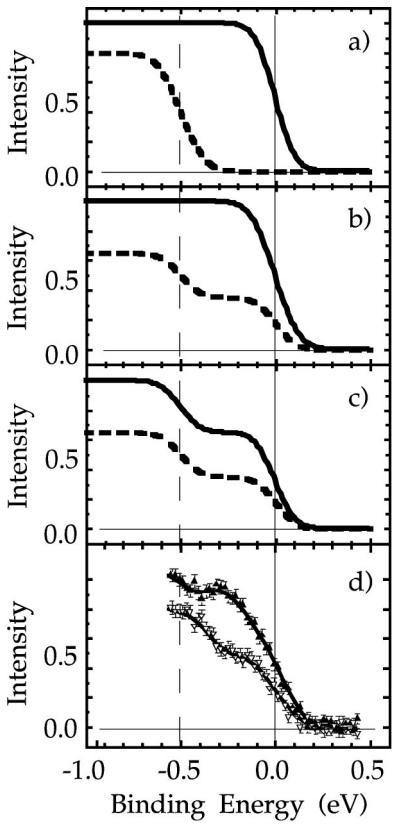

FIG. 4. Schematic representation of the spin-resolved photoemission measurements from (a) ideal HMF films, (b) HMF with nonmagnetic component, and (c) HMF film with low remnant magnetization. (d) Measured data from NiMnSb with 38 eV photons. Spin-majority and spin-minority spectra are shown as full and dashed lines in (a)–(c), and as ▲ and ▽ in (d), respectively.

are not exchange split but originate from different features in SRDOS instead. More likely, the exchange split features are the minority-spin peak at ~ 1.7 eV and the higher binding energy majority-spin feature at 3.0 eV yielding an exchange splitting of ~ 1.3 eV. It can be also noticed that the 3.0 eV peak observed in the spin-integrated spectrum [Fig. 1(c)] is of predominantly majority-spin character. All of the above observations are in good agreement with calculated SRDOS.[15] The low binding energy shoulder ($E_b \sim 0 - 1.2$ eV) on the other hand shows a spin polarization of only $\sim 15\%$.

In order to better understand the roles the constituent elements play in the NiMnSb alloy, we performed resonant SRPES measurements at the Mn and Ni photoexcitation edges. The spectra taken at the Mn-M_{23} *antiresonance* [$h\nu = 52$ eV; see Fig. 2(b)] shows an overall decrease in spin polarization, as compared to the off-resonance spectra [Fig. 2(a)], suggesting that the local Mn-DOS is the main source of the electron spin polarization. We also observe an appreciable decrease in the majority peak at 3.0 eV indicating its origin to be primarily of local Mn $3d$ character. Both of these facts are consistent with theoretical predictions.[15] The spectra taken at the Ni-M_{23} *resonance* [$h\nu = 76$ eV; see Fig. 2(c)], on the other hand, show both spin components of the 3.0 eV present, indicating that this feature also has a contri-

bution from local Ni 3*d* orbitals. It is interesting to note that the minority-peak appears at somewhat higher binding energy than the majority one contrary to the usual order of exchange split features but in agreement with the projected local (Ni) SRDOS from Ref. 15 (not shown in Fig. 2). We also note that the spin splitting of the main peak at 1.7 eV is less pronounced at the Ni *resonance* [Fig. 2(c)] than in the *off-resonance* spectra [Fig. 2(a)] suggesting different binding energies for the Ni and Mn-DOS maxima. All of the above observations made from measured spectra agree well with calculations of Youn and Min,[15] which we take as a further indication that the surface region of our films is NiMnSb-like.

We now turn to the issue of the spin polarization of the states close to the Fermi level and the question whether NiMnSb is HMF. The spin-resolved photoemission intensity presented in Figs. 2(a)–2(c) all show the spin polarization to be considerably smaller (15–40 %) than expected 100% for the HMF. The largest polarization is observed at the Ni-M_{23} *resonance* and this data is replotted as spin polarization $[(I_{up}-I_{down})/(I_{up}+I_{down})]$ in Fig. 3(a). Although the magnitude of the measured polarization throughout the spectrum is smaller than the one predicted, the shape of polarization curve is similar to the one calculated from data in Ref. 15, and shown in Fig. 3(b). In particular, a pronounced minimum at 1.7 eV and steep increase at close to the predicted spin gap energy ($E_{gap}=0.5$ eV) is clearly observed in the measurement. This large enhancement in polarization at ~ 0.5 eV (by a factor of 2 going from below to above E_{gap}) is observed at all three photon energies and it is consistent with the theoretical predictions. We take this as an indication of the presence of a surface phase that exhibits half-metallic behavior.

In order to reconcile the observation of less than 100% spin polarization and the observation of E_{gap} of HMF phase we now turn to more detailed examination of the spin-resolved NiMnSb spectra close to Fermi level, as shown in Fig. 4(d). There are at least two plausible explanations for this discrepancy. They are depicted schematically in Figs. 4(b) and 4(c), starting from ideal HFM [Fig. 4(a)] and assuming a flat DOS in first 1 eV below the Fermi level. The most obvious cause is the presence of another phase at the surface of NiMnSb. A nonmagnetic metallic phase would add an equal strength to the majority- and minority-spin components, effectively decreasing the polarization within the spin gap [Fig. 4(b)]. The other plausible explanation is low surface remnant magnetization, which would lead to mixing of the two spin spectra as shown in Fig. 4(c). In both cases it is clear that in spite of lower than 100% spin polarization it is still possible to identify the onset of the spin gap (indicated by the dashed vertical line). We submit that our measurements are consistent with such scenarios, although it is not possible to estimate relative contribution of the two.

In conclusion, we show that it is possible to prepare the surface of NiMnSb to exhibit spin-resolved electronic structure close to the bulk one, in a good agreement with calculated SRDOS.[15] This is similar to conclusion reached by recent spin-resolved inverse-photoemission measurements performed on NiMnSb/Mo/MgO(001) films.[16] Our data show a large increase in electron spin polarization at the 0.5 eV below the Fermi level, suggesting the presence of half-metallic ferromagnet (HMF) phase. The maximum observed spin polarization of only 40% is interpreted as due to other phases and/or lower surface magnetization. Although this value is smaller than the one predicted for HMF, it is considerably higher than 15% deduced from the MR measurements.[6] This suggests that with more elaborate surface preparation and/or *in situ* NiMnSb film growth it may be possible to generate surface regions with much higher electron spin polarization which would be useful for application in magnetoresistive devices.

[1] J. S. Moodera, Lisa R. Kinder, Terrilyn M. Wong, and R. Meservey, Phys. Rev. Lett. **74**, 3273 (1995).
[2] S. S. P. Parkin *et al.*, J. Appl. Phys. **85**, 5828 (1999).
[3] J.-H. Park, E. Vescovo, H.-J. Kim, C. Kwon, R. Ramesh, and T. Venkatesan, Nature (London) **392**, 794 (1998).
[4] R. A. de Groot and F. M. Mueller, Phys. Rev. Lett. **50**, 2024 (1983).
[5] R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, J. Appl. Phys. **55**, 2151 (1984).
[6] C. T. Tanaka, J. Nowak, and J. S. Moodera, J. Appl. Phys. **81**, 5515 (1997).
[7] R. Jansen and J. S. Moodera, J. Appl. Phys. **83**, 6682 (1998).
[8] R. J. Soulen *et al.*, Science **282**, 85 (1998).
[9] G. L. Bona, F. Meier, M. Taborelli, E. Bucher, and P. H. Schmidt, Solid State Commun. **56**, 391 (1985).
[10] D. Oberli, R. Burgermeister, S. Riesen, W. Weber, and H. C. Siegmann, Phys. Rev. Lett. **81**, 4228 (1998).
[11] R. Kabani, M. Terada, A. Roshko, and J. S. Moodera, J. Appl. Phys. **67**, 4898 (1990).
[12] E. Vescovo, H.-J. Kim, Q.-Y. Dong, G. Nintzel, D. Carlson, S. Hulbert, and N. V. Smith, Synchrotron Radiat. News **12**, 10 (1999).
[13] J.-S. Kang, J. H. Hong, S. W. Jung, Y. P. Lee, J.-G. Park, C. G. Olson, S. J. Yong, and B. I. Min, Solid State Commun. **88**, 653 (1993).
[14] S. W. Rogey, L. T. Hudson, and R. L. Kurtz, Phys. Rev. B **46**, 11 697 (1992).
[15] S. J. Youn and B. I. Min, Phys. Rev. B **51**, 10 436 (1995).
[16] D. Ristoiu, J. P. Nozíeres, C. N. Borca, T. Komesu, H.-k. Jeong, and P.A. Dowben, Europhys. Lett. **49**, 624 (2000).