JOURNAL OF APPLIED PHYSICS **99**, 073710 (2006)

Anomalous metal-to-insulator transition in FeSi films deposited on SiO_2/Si substrates

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(Received 15 November 2005; accepted 7 February 2006; published online 13 April 2006)

In-plane conductivity measurements of FeSi films deposited on boron-doped silicon substrates exhibited an anomalous metal-to-insulator transition near 250 K. In the temperature range of 250–215 K the resistance of the films increased by more than three orders of magnitude. For temperatures >250 K, metallic conductivity consistent with the conductivity of the doped silicon substrate was observed. This indicates an ohmic contact between the film and the silicon substrate across the native SiO_2 layer. Below the transition temperature (<250 K), the temperature dependence of the resistance implies hopping conduction between localized states that is observed in disordered FeSi films. This metal-to-insulator transition observed in these films suggests switching of the current percolation path from substrate to the film due to a rapid increase in the interfacial resistance. The experimental results agree well with a three-layer model that incorporates an exponentially increasing interfacial resistance with decreasing temperature. The presence of a thin native oxide layer between the deposited film and the silicon substrate is essential for manifestation of the transition. Cross-sectional transmission electron microscopy analysis indicated diffusion of Fe through the oxide barrier and accumulation of Fe at the SiO_2/Si interface. The band bending at the interface resulting from Fermi level pinning due to interface states and the formation of $(Fe^{+/++}B^{-})^{0/+}$ pairs at the SiO_2/Si interface may be responsible for the observed transition. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2185831]

I. INTRODUCTION

Electrical and magnetic investigations of single-crystal samples of FeSi have revealed unusual transport properties at both low and high temperatures. The magnetic susceptibility of FeSi has been observed to rise rapidly above 100 K up to a maximum at 500 K.[1] The semiconducting properties of FeSi are characterized by a narrow indirect band gap between 0.05 and 0.11 eV.[1] The resistivity of FeSi at room temperature is in the range of 140–280 $\mu\Omega$ cm, and has been shown to gradually increase by about three orders of magnitude between 200 and 30 K.[2] The exact mechanism responsible for the unusual temperature-dependent electrical and magnetic behavior of FeSi is still ambiguous. Several theoretical interpretations including thermally induced intermediate valance states of Fe, and dirty Kondo insulating behavior[3] have been presented. Thin films of FeSi have also been grown on atomically cleaned Si substrates.[4] A study of the conduction properties of these films in the temperature range of 290–400 K reported metallic behavior characterized by hole conductivity.[5]

Past investigations of FeSi and $FeSi_2$ films have been exclusively on films grown directly on silicon substrates.[4,5] The interaction of Fe films with Si substrates across a thin native SiO_2 layer has also been well studied.[6] The high diffusivity of Fe in SiO_2 and Si has been well documented to be one of the failure mechanisms of metal-insulator-semiconductor (MIS) device elements when Fe is present as a contaminant.[7] Several analytical techniques have been used to probe the interfacial diffusion and reactions in the $Fe/SiO_2/Si$ structures. Auger spectroscopy studies conducted on room temperature deposited Fe films on bare Si and on Si with a native SiO_2 layer have revealed the formation of FeSi at the Fe–Si interface of the Fe/Si system while formation of FeSi was suppressed by the presence of the oxide layer in SiO_2/Si system. However, heating above 450 °C resulted in forming FeSi and $FeSi_2$ at the SiO_2–Si interface.[8] Based on the thermodynamic analysis of transition metal-SiO_2 reaction kinetics a correlation between silicide formation at 800 °C and the electronegativity of the metal has been made.[9] Metals with electronegativity below 1.5 on the Pauling scale will react with SiO_2. Based on this criterion Ti and V react to form silicides while Fe, Co, and Ni will not. Hofmann *et al.*[10] investigated the interfacial reactivity of rare-earth metals (R), such as Pr, Eu, Gd, and Yb, deposited onto ultrathin films of SiO_2 on top of Si substrates. They observed the rapid reaction of the rare-earth metal with the insulating SiO_2 layer at room temperature to form metal silicides and oxides, thereby reducing the SiO_2.

This paper presents the results of our investigation of FeSi films deposited by laser ablation on silicon substrates with intact native oxide layers. These films exhibited unusual electrical characteristics resembling a metal-to-insulator transition that was accompanied by a change in resistance of more than three orders of magnitude. This is in contrast to similar behavior with only 50% change in resistance in Cu and Co films deposited on silicon substrates that have been reported previously.[11] These observations have been attrib-

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0021-8979/2006/99(7)/073710/5/$23.00

uted to the formation of an inversion layer at the surface of the silicon substrate. The present study is aimed at understanding the role of the FeSi/SiO_2/Si interfaces on the manifestation of this transition.

II. EXPERIMENT

A. Film growth

In our study FeSi films were deposited on *p*-type doped silicon substrates using a laser ablation process. A commercial FeSi target was ablated by an excimer laser operated at a wavelength of 248 nm with pulses of 200 mJ energy and 30 ns in duration. The laser fluence at the target was about 3 J/cm^2. Boron-doped silicon substrates of resistivity in the range of 1–10 Ω cm were used in all experiments. Standard solvent cleaning techniques were used to prepare substrates for deposition. The native SiO_2 layer on silicon, which was about 20–40 Å in thickness, was not removed prior to film growth. The deposition was carried out in a pressure of about 10^{-6} torr. Under these deposition conditions the growth rate of the film was approximately 1 Å per pulse. The typical thicknesses of the films investigated in this study were about 600 Å. The status of the FeSi/SiO_2 and SiO_2/Si interfaces, and the diffusion of Fe across the interface were studied by cross-sectional transmission electron microscopy (TEM) analysis.

B. Electrical characterization

The temperature dependence of the in-plane conductivity of the films was measured by a four-point probe technique. The currents used were in the range of 1–100 μA. A closed cycle refrigeration system was used to control the temperature of the samples within a degree during the measurements. Two separate techniques were used to make low resistivity contacts to the film. In one method, thin indium pads were pressed on to the film followed by fixing the probes onto the pad by silver paint. In the other method, the probes were fixed directly onto the film by silver paint. At each temperature ten voltage measurements were made for a fixed current. No significant difference in the average voltage measurements using the two types of contacts was observed. However, indium contacts produced less noise, indicated by the smaller standard deviation of the voltage measurement.

III. RESULTS AND DISCUSSION

A. Electrical properties

The temperature dependence of the measured resistance of a FeSi film deposited at a silicon substrate temperature of 400 °C is shown in Fig. 1. The film showed metallic behavior at high temperature and underwent a transition at 270 K to a highly resistive state. The film resistance changed from 40 Ω at 270 K to 1×10^4 Ω at 230 K, followed by a gradual increase in resistance down to 50 K. This behavior is quite different from the resistivity results reported in the literature for FeSi.[2,4] Clearly, the presence of the thin SiO_2 layer between the film and the silicon substrate plays a major role in the manifestation of the observed anomalous transition in film resistance. Figure 1 also includes the temperature dependence of FeSi film deposited on an insulating sapphire substrate (curve b). For comparison, the temperature dependent resistance of a *p*-type bare silicon substrate was measured by etching the native SiO_2 layer using HF vapor and making ohmic contacts to the substrate (curve c). The room temperature resistivity of the substrate was 1–10 Ω cm, which corresponds to a boron doping concentration of $\sim10^{17}$ cm^{-3}. This behavior of the silicon substrate is consistent with the results reported in the literature for highly doped silicon.[12] Comparison of the three curves in Fig. 1 suggests that the conductivity of the film at high temperature mimics that of the silicon substrate whereas the conductivity below the transition temperature is closer to that of an isolated FeSi film.

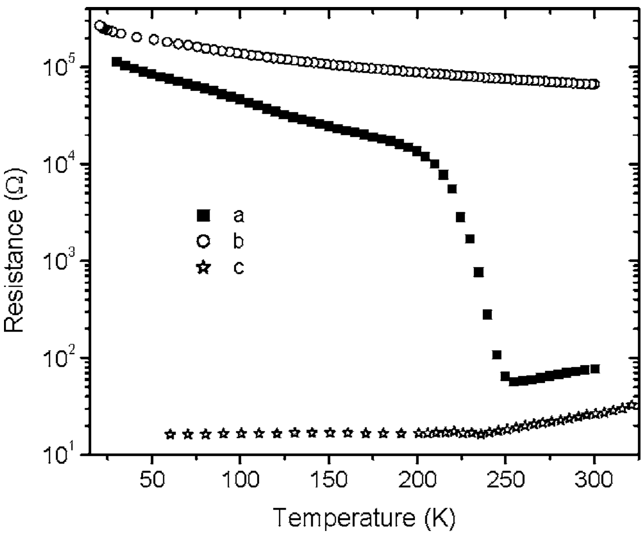

FIG. 1. Temperature dependence of the resistance of FeSi films deposited at 400 °C on (a) *p*-type silicon substrate of resistivity 1–10 Ω cm, (b) sapphire substrate. Curve (c) shows the temperature dependence of resistance for the etched silicon substrate.

The *I-V* characteristics of the film derived from four-point-probe measurements are shown in Fig. 2. The linear behavior above the transition temperature [Fig. 2(a)] supports the argument that the film makes an ohmic contact to the silicon substrate across the SiO_2 layer at high temperature, and thus, the current is transported through the substrate. However, as shown in Fig. 2(b) the current transport becomes nonlinear just below the transition temperature indicating a change in the transport mechanism. The *I-V* curve resembles that of a reverse biased nonideal diode. As shown in Fig. 3 the experimental results fit closely to a functional form of $I=[c(d+V)]^{1/3}$, where c and d are constants. This nonlinear behavior can be explained by considering a generation-recombination mechanism for carrier transport at the interface. Under equilibrium conditions the states at the SiO_2/Si interface cause the Fermi level to be pinned leading to a built-in potential of V_{bi}. For an abrupt junction with an impurity density of N the depletion layer width in *p*-silicon can be written in the form[13]

$$W=\sqrt{\frac{2\varepsilon}{qN}\left(V_{\mathrm{bi}}-V-\frac{kT}{q}\right)},$$

where ε is the permittivity of the semiconductor, q is the electron charge, and T is the temperature. The impurity con-

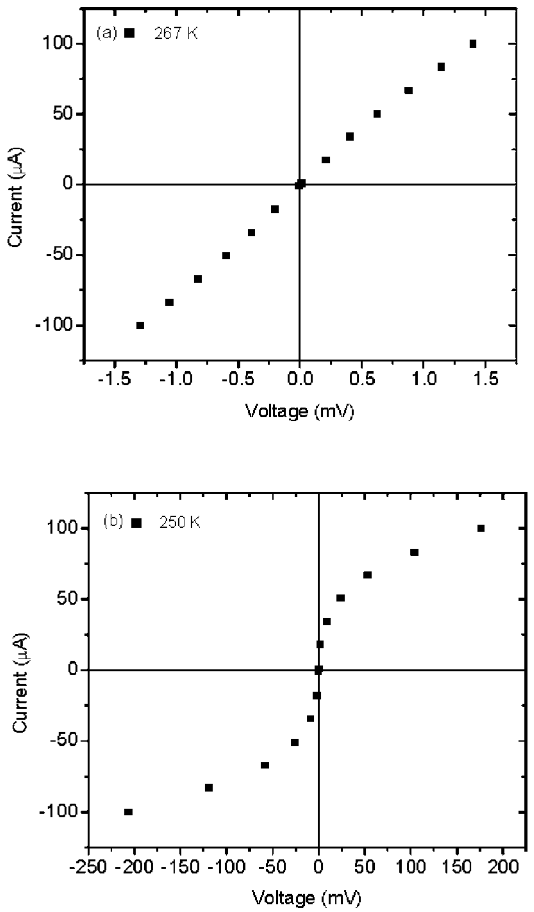

FIG. 2. *I*-*V* characteristics of the a FeSi film deposited at 400 °C on *p*-type silicon at the temperatures of (a) 267 K, before the transition, (b) 250 K, on set of the transition.

centration near the interface is altered by the diffusion of Fe into silicon. For a linearly graded junction the depletion layer width becomes

$$W=\left[\frac{12\varepsilon}{qa}\left(V_{\mathrm{bi}}-V-\frac{kT}{q}\right)\right]^{1/3},$$

where a is the impurity gradient. If carrier transport across the depletion layer takes place by capture and emission by localized impurity states, the recombination rate U can be written as $U=N_i/\tau$ where N_i is the intrinsic carrier density and τ is the effective lifetime of the carriers. The generation-recombination current density due to all the impurity states in the depletion layer is given by

$$J=\int_0^W qUdx,$$

$$J=\frac{qNW}{\tau}\sim\left(V_{\mathrm{bi}}-V-\frac{kT}{q}\right)^{1/3}.$$

At reverse bias,

$$J\sim\left(V_{\mathrm{bi}}+V-\frac{kT}{q}\right)^{1/3}.$$

The nonlinear *I*-*V* characteristic of the film observed below the transition temperature agrees well with the voltage dependence of current described by this generation-recombination mechanism.

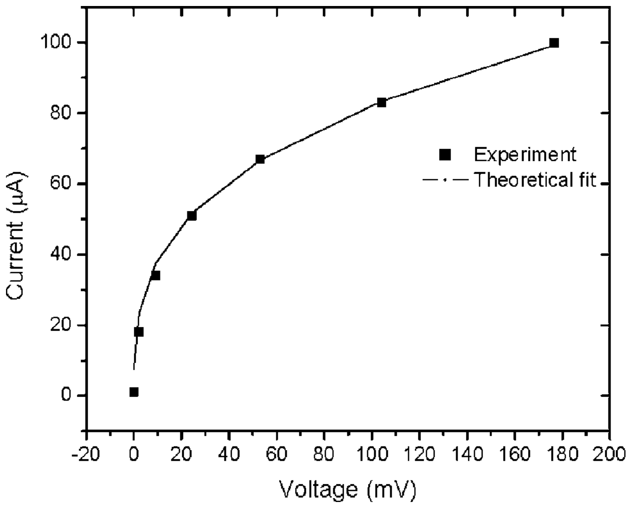

FIG. 3. Comparison of the experimental data from *I*-*V* curve in Fig. 2(b) and the theoretical fit. The *I*-*V* characteristics change from linear to nonlinear at the temperature of 250 K.

B. Effect of substrate temperature

The observed transition indicates that at high temperatures a majority of the charge carriers are transported across the SiO_2 layer to the silicon substrate with very low resistance resulting in conduction through the substrate. At the transition temperature, the resistance of the interface layer increases rapidly forcing the current transport to be confined primarily to the film. Such a mechanism governed by the interface states should depend on the nature of the interface. The effect of interface diffusion on the transition was investigated by depositing films of similar thickness at higher temperatures. The temperature dependence of the resistance for films grown at room temperature, 400 and 900 °C are shown in Fig. 4. The highest change in resistance and the narrowest transition width was observed for the room-temperature deposited film. Increasing substrate temperature led to the broadening of the transition with a reduction in its magnitude.

C. Interface stoichiometry analysis

X-ray-diffraction studies of the films deposited at room temperature, 400, and 900 °C, failed to identify the presence of any crystalline phases, indicating that FeSi structures with any long-range order are not formed at any temperature. The film/substrate interface of a thin FeSi film deposited at 450 °C was probed by TEM with energy dispersive x-ray spectroscopy (EDX) analysis to ascertain the degree of interfacial diffusion and the integrity of the SiO_2 layer. As seen in the TEM image in Fig. 5, the SiO_2 layer has a thickness of about 30–40 Å. The EDX profile across the film (Fig. 6) indicates a 1:1 ratio of Fe:Si throughout the film. A significant degree of Fe diffusion through the SiO_2 layer into the

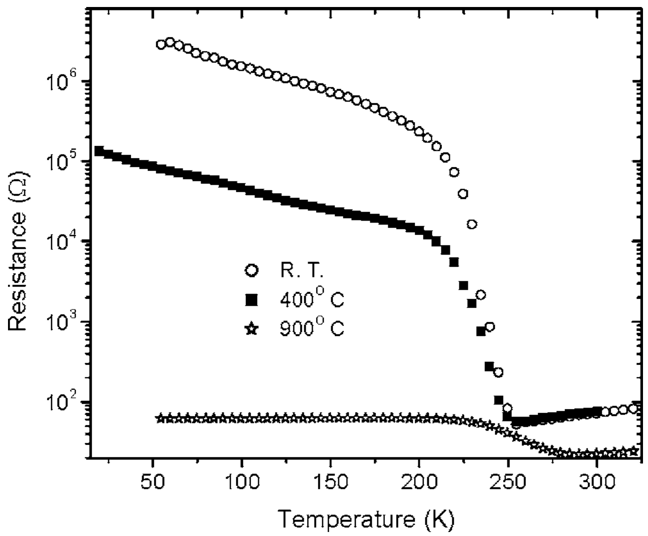

FIG. 4. Temperature dependence of the normalized resistance of FeSi films deposited on silicon substrates at growth temperatures of (a) room temperature, (b) 400 °C, and (c) 900 °C.

substrate is noticeable in this image. In addition, Fe signal indicating a possible accumulation of Fe at the SiO_2–Si interface is visible.

IV. A THREE-LAYER MODEL

The results presented in Fig. 1 support the concept that at high temperature the thin SiO_2 interface layer has a very low resistance to the current carriers and thus most of the current is transported through the silicon substrate. With reducing temperature the current is shifted from silicon to the FeSi film. We have used a three layer model to describe the metal-to-insulator transition observed in these films. This model considers a network (Fig. 7) of resistors that represent the resistances of the FeSi film, SiO_2 interface layer, and the silicon substrate. The functions that represent the temperature dependence of resistances for the FeSi film $[r(T)]$, and silicon $[\rho(T)]$, were obtained from the experimental data in Fig. 1. The resistance between the two voltage leads in the network (R), which is the measured value in four-point-probe measurements, can be expressed in terms of $r(T)$, $\rho(T)$, and the interface layer resistance $q(T)$,

$$R = \frac{2r[q(\rho+q)]+\rho r(\rho+r+2q)}{\rho^2+r^2+2q^2+4rq+2\rho(r+2q)}.$$

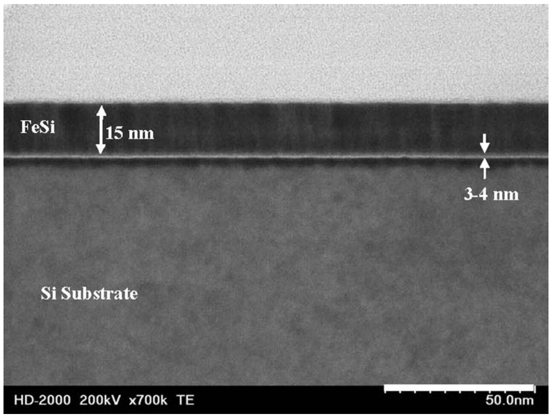

FIG. 5. Transmission electron micrograph (TEM) of the interface between a FeSi film and the silicon substrate. The film was deposited at 400 °C. The thicknesses of the FeSi film and the SiO_2 layer are indicated on the image.

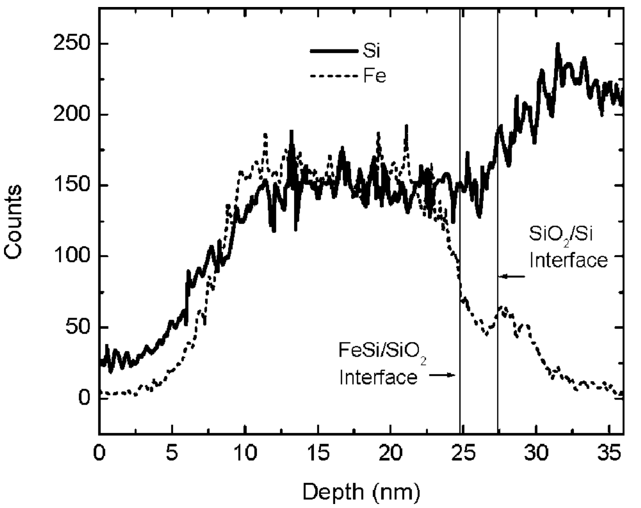

FIG. 6. EDX analysis of the Fe and Si composition variation along a cross section of the film. Position of the film/SiO_2 and SiO_2/Si interfaces are indicated in the figure.

A close agreement between the experimental results and a theoretical fit based on Eq. (1) is shown in Fig. 8 for an interlayer resistance of $q(T)=\alpha\exp(\varepsilon/kT)$ with $\alpha=1.25\times10^{-9}$ Ω and $\varepsilon=0.54$ eV.

V. CONCLUSION

In the absence of sufficient thermal energy the laser-ablated films deposited at room temperature are expected to be amorphous. Previous work published by other researchers on surface analysis of Fe films on SiO_2/Si substrates has presented evidence for Fe diffusion through the SiO_2 layer even for room temperature growth.[14] Physical and chemical changes taking place at the film/SiO_2 and SiO_2/Si interfaces due to Fe diffusion will affect the majority carrier transport across the thin insulating SiO_2 layer. Diffusion of iron into the SiO_2 layer in its multiple valance states, Fe^0, Fe^+, and Fe^{++} will form an impurity band within the large band gap of the insulator. Similar high conductivity through such impu-

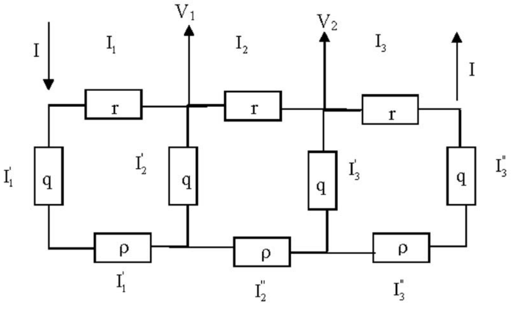

FIG. 7. Resistor network used in the three-layer model. The parameters r, q, and ρ represent the resistance corresponding to the film, the interface, and the Si substrate, respectively.

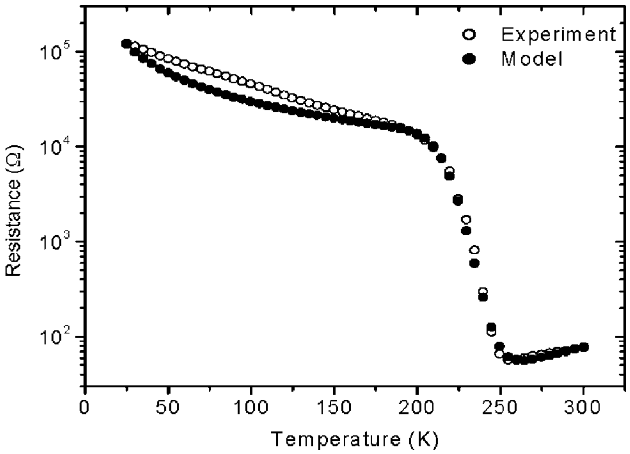

FIG. 8. Comparison of the experiment and the three-layer model for the temperature dependence of the film resistance.

rity bands in insulators due to electron hopping between different valancy states are observed in transition-metal doped glass.[15] Diffusion of iron into silicon, as observed in TEM analysis, will also alter the band bending at the SiO_2/Si interface.[10] A similar effect was demonstrated by Xu *et al.*[16] where the deposition of a thin film of Au on a 20–50-Å-thick CaF_2 film grown on a *p*-type Si substrate was shown to alter the electrical properties at the CaF_2/Si interface leading to changes in valence-band offset. It is known that Fe produces a donor level in boron doped *p*-type silicon.[17] Presence of Fe^+ and Fe^{++} at the silicon interface will change band bending at the interface. At room temperature delocalized carrires may hop through impurity ions in the depletion layer with low resistance for carrier transport. Furthermore, formation of $(F^{+/++}B^-)^{0/+}$ pairs due to coulomb interaction between substitutional B^- and interstitial $Fe^{+/++}$ ions is also well documented. Formation of pairs is a thermally activated process, the density of pairs being proportional to $\exp(E_b/kT)$, where E_b is the binding energy of the pair. Values reported for E_b in the literature range from 0.53 to 0.65 eV.[18] As the Fe ions increasingly form pairs with decreasing temperature, electrons may become localized and the hopping probability will decrease leading to an increase in the resistance to carrier transport. The functional behavior of the interface resistance, $q \propto \exp(E/kT)$, derived from the three layer model describes a thermally activated conduction mechanism for the conduction across the interface with an activation energy of 0.54 eV, which is in the range of binding energies reported for the FeB pair formation.

In summary, the anomalous behavior of temperature-dependent electrical transport properties of thin FeSi films deposited on *p*-doped Si substrates with a native oxide layer has been presented. The film makes an ohmic contact to the Si substrate through the SiO_2 layer down to a temperature of 250 K, followed by more than three orders of magnitude change in resistivity in the temperature range of 250–215 K. TEM analysis of the SiO_2/Si interface and the effect of the film growth temperature on the metallic to insulator transition suggest that the diffusion of Fe into the SiO_2/Si interface is responsible for the transition. A three-layer model that incorporates a thermally activated transport mechanism at the SiO_2/Si interface agrees well with the experimental results.

This work was supported in part by the National Science Foundation under Grant Nos. DMI-0217939 and DMI-0078917.

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