

Electrical and Thermal Conduction in Atomic Layer Deposition Nanobridges Down to 7 nm Thickness

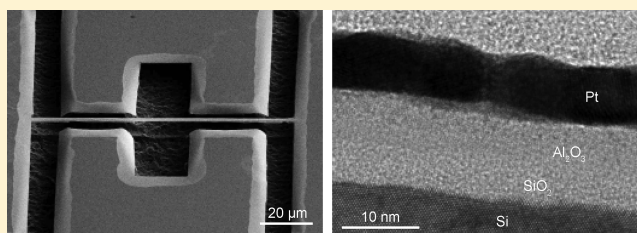
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ABSTRACT: While the literature is rich with data for the electrical behavior of nanotransistors based on semiconductor nanowires and carbon nanotubes, few data are available for ultrascaled metal interconnects that will be demanded by these devices. Atomic layer deposition (ALD), which uses a sequence of self-limiting surface reactions to achieve high-quality nanolayers, provides an unique opportunity to study the limits of electrical and thermal conduction in metal interconnects. This work measures and interprets the electrical and thermal conductivities of free-standing platinum films of thickness 7.3, 9.8, and 12.1 nm in the temperature range from 50 to 320 K. Conductivity data for the 7.3 nm bridge are reduced by 77.8% (electrical) and 66.3% (thermal) compared to bulk values due to electron scattering at material and grain boundaries. The measurement results indicate that the contribution of phonon conduction is significant in the total thermal conductivity of the ALD films.

KEYWORDS: Atomic layer deposition, electrical conductivity, Lorenz number, platinum, size effect, thermal conductivity



Frontier nanoelectronics research features electron transport studies in metallic and semiconductor nanowires, carbon nanotubes, and related low-dimensional structures.^{1–3} However, the limiting behavior of ultrascaled thin-film metallic interconnects has received relatively little attention, in part because of the challenge of sample preparation for the sub 10 nm regime. The challenge is particularly great for thermal transport measurements, which are important for reliability and self-heating predictions, because accurate data require a free-standing bridge structure to minimize heat losses by the parasitic transport in the substrate.⁴ The microfabrication process of such structures is not mature for sub 10 nm thick metal films. The Wiedemann–Franz law (WFL) can estimate the total thermal conductivity of metals from electrical conductivity data with assuming that the phonon thermal conductivity κ_{ph} is sufficiently small. However, the prediction based on the WFL fails in ultrathin and defective metal films due to inelastic scattering and the phonon conduction.^{5,6} A detailed study of both electrical and thermal transport in metal nanobridges in the sub 10 nm regime is overdue.

This Letter reports and interprets independent measurements of the electrical and thermal conductivities of free-standing platinum (Pt) nanobridges in the temperature range from 50 to 320 K. The films of thickness 7.3, 9.8, and 12.1 nm are fabricated using atomic layer deposition (ALD), which uses a sequence of self-limiting surface reactions.⁷ ALD is highly relevant to integrated circuits and microelectromechanical systems because of the excellent conformality, thickness uniformity, and precise thickness control.^{8,9} Several researchers

have recently demonstrated free-standing ALD-grown structures for microelectromechanical switches and microbolometers,^{10,11} but there is not yet data for the electrical and thermal transport.

The fabrication process of free-standing Pt films starts from a silicon (Si) (100) wafer. An amorphous aluminum oxide (Al_2O_3) film with the thickness of 5–10 nm is formed by ALD at 250 °C using trimethylaluminum [$\text{Al}(\text{CH}_3)_3$] and water as precursors.^{12,13} A Pt film is then deposited at 250 °C from (methylcyclopentadienyl)trimethylplatinum [$(\text{CH}_3\text{C}_5\text{H}_4)\text{Pt}(\text{CH}_3)_3$] and oxygen.¹⁴ The Al_2O_3 layer enhances the nucleation of Pt and provides electrical insulation between the Pt layer and the substrate.¹⁴ Both layers are patterned with ion milling. The devices are released by etching the Al_2O_3 layer with a dilute (1%) hydrofluoric acid (HF) solution followed by xenon difluoride vapor etching of Si. Figure 1 shows the scanning electron microscope (SEM) and cross-sectional transmission electron microscope (TEM) images of the fabricated samples. The length l and width w of the samples have several variations ($l = 100, 200 \mu\text{m}$ and $w = 2, 4 \mu\text{m}$). The Pt film thicknesses h (7.3, 9.8, and 12.1 nm) are controlled by the number of ALD cycles and verified by TEM. Characterization using X-ray diffraction confirms that the crystal plane of the Pt films is well aligned in (111) direction as a previous report.¹⁴

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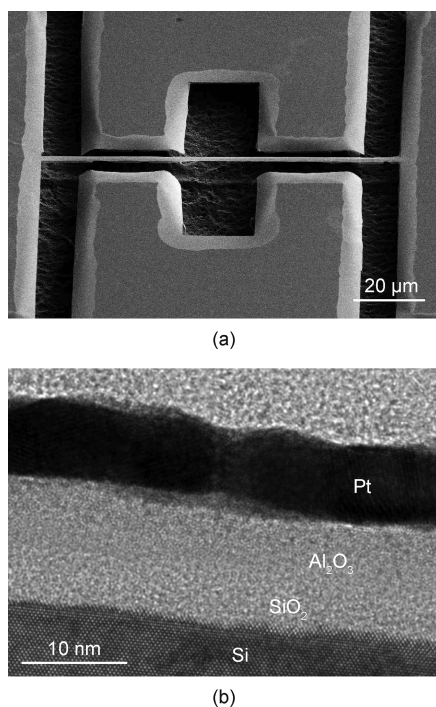


Figure 1. (a) SEM image of the free-standing Pt film tilted by 50°. (b) Cross-sectional TEM image of the ALD Pt film. The lighter contrast amorphous layer between Al_2O_3 and Si is native silicon dioxide (SiO_2).

The electrical and thermal conductivities are measured simultaneously at each temperature using wire-bonded samples mounted on a ceramic package with a silicon diode temperature sensor. The electrical conductivity and the temperature coefficient of the resistance (TCR) are measured with a low current to ensure negligible Joule heating ($\leq 5 \mu\text{A}$). The thermal conductivity is measured using harmonic Joule heating and electrical resistance thermometry.¹⁵ The bridge transmits current at angular frequency ω and causes temperature (and electrical resistance) oscillations at 2ω , which together yield a 3ω voltage component that is proportional to the temperature amplitude in the bridge. The 3ω component (extracted using a differential amplifier circuit and a lock-in amplifier) and the TCR yield the lengthwise average temperature along the bridge, from which the solution to the heat conduction equation yields the in-plane thermal conductivity. Heat losses along the bridge are negligible, and the use of continuum heat conduction analysis in the in-plane direction is justified because the bridge length far exceeds the electron mean free path. This study uses low-frequency data ($<100 \text{ Hz}$) for which the impact of the wire heat capacity is negligible.

Figure 2 shows the thickness-dependent electrical and thermal conductivities of ALD Pt films at 300 K. The error bars in Figure 2 include the uncertainty in the Pt thickness and the effect of the Al_2O_3 layer on the free-standing film after HF etching. The upper and lower limits of the total measurement errors in the thermal conductivities are less than 9 and 17%. Since the reported thermal conductivity of amorphous Al_2O_3 is around $1.6 \text{ W/(K}\cdot\text{m)}$,^{16,17} the uncertainty of measured thermal conductivities due to the Al_2O_3 layer is less than 9% even if the entire layer remains. Both the electrical and thermal conductivities of the ALD Pt films are significantly smaller than their bulk values. This is consistent with a number of reports in literature where the film thickness is comparable with

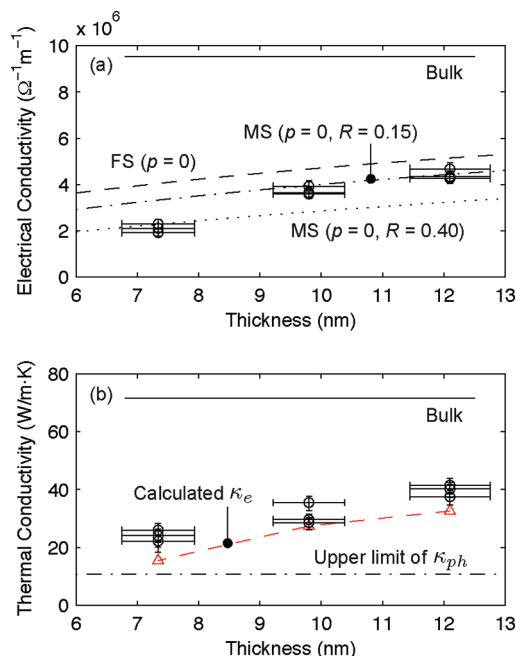


Figure 2. Thickness dependence of (a) electrical and (b) thermal conductivities of Pt films at 300 K. The solid lines are the bulk values. The dash line in (a) is the lower bound of the FS model, and the dash-dot and dot lines are based on the MS model. The dash-dot line in (b) is the κ_{ph} of bulk Pt.³¹

or smaller than the electron mean free path (MFP) of bulk Pt at 300 K ($\sim 22.4 \text{ nm}$).^{18–21} The Fuchs–Sondheimer (FS) model captures the conductivity reduction in thin films as a function of the surface specular reflection coefficient p by accounting for the electron surface scattering.^{22,23} Figure 2a shows that the measured electrical conductivities are smaller than the lower bound of the FS model where the surface is completely diffuse ($p = 0$). This implies that additional scattering sources are important in the Pt films. The electrical conductivities are then compared with the Mayadas–Shatzkes (MS) model, which incorporates the grain boundary scattering.^{24,25} The dash and dash-dot lines in Figure 2a show the predictions of the MS model. The completely diffuse surface is assumed because the electron wavelength in Pt ($\sim 0.4 \text{ nm}$) is smaller than the average roughness of the Pt films ($\sim 1 \text{ nm}$). The lateral grain size d in the MS model is approximated as $d = 1.5h$ based on the TEM observations. It is found that the MS model using a constant grain boundaries reflectivity coefficient R does not capture the thickness dependence among the ALD Pt films, unlike the previous studies in metal films with the thickness of 8.5–1000 nm.^{25–27} While the 9.8 and 12.1 nm Pt films agree with the MS model for $R = 0.15$, the 7.3 nm Pt film matches well for $R = 0.40$. The discrepancy can be due to the density variation of the Pt films with different thicknesses. At the initial stage of ALD process, the density of the Pt film increases with the increase of the film thickness until it reaches to the bulk value.^{28,29} The discontinuity of thin films can increase the R . This indicates that the MS model might have to account for the variation of density in the ALD films.

The average Lorenz numbers L based on the measured thermal conductivities are 3.82×10^{-8} , 2.79×10^{-8} , and $2.99 \times 10^{-8} \text{ V}^2/\text{K}^2$ for 7.3, 9.8, and 12.1 nm Pt films, respectively. These values are larger than the Sommerfeld value $L_0 = 2.45 \times 10^{-8} \text{ V}^2/\text{K}^2$.⁵ To investigate the disparity, electron thermal

conductivity κ_e is calculated using the WFL $k_e = L_0 T \sigma$, where T is the absolute temperature and σ is the measured electrical conductivity.⁵ Figure 2b compares the measured thermal conductivities and the calculated κ_e . Their differences may correspond to the κ_{ph} since the total thermal conductivity is the sum of the κ_e and κ_{ph} .³⁰ The estimated κ_{ph} is lower than the bulk κ_{ph} that is derived from the molecular dynamics simulation.³¹ Figure 2b shows the contribution of κ_{ph} in the total thermal conductivity can be important especially for the 7.3 nm Pt film. The increased contribution of κ_{ph} explains the large L found in the ALD Pt films.

The temperature dependence of electrical and thermal conductivities of the Pt films is shown in Figure 3. The

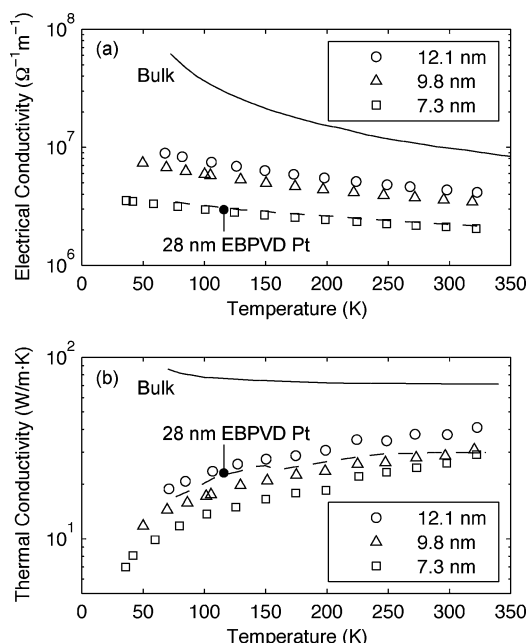


Figure 3. Temperature dependence of (a) electrical and (b) thermal conductivities of Pt films with 7.3, 9.8, and 12.1 nm thicknesses. The solid lines are the bulk values. The dash lines show the electrical and thermal conductivities of the 28 nm EBPVD Pt film.¹⁸

measurement uncertainties of the electrical and thermal conductivities due to the uncertainties in the Pt thicknesses are less than $\pm 9\%$. While the electrical conductivity shows similar temperature dependence to the bulk over the measured temperature range, the thermal conductivity exhibits opposite temperature dependence with the bulk and increases with the temperature rise. The observed temperature dependence is consistent with the results in earlier studies for nanometer-thick metal films and metal nanowires.^{18,32} Because the electron scattering with imperfections is dominant in the ALD Pt films, the electrical and thermal conductivities behave as T^0 and T , respectively.

The measured conductivities are compared with the previous studies of a 28 nm Pt film formed by electron beam physical vapor deposition (EBPVD), as shown in Figure 3.¹⁸ The electrical conductivity of the 28 nm EBPVD Pt film is similar with the 7.3 nm ALD Pt film, which suggests that the EBPVD Pt film contains more grain boundaries, imperfections, or impurities in crystals. Additionally, the 28 nm EBPVD Pt film has larger thermal conductivity than the 7.3 nm ALD Pt film, which is possible when the κ_{ph} is larger for the 28 nm film.

Electrical and thermal conductivities of free-standing Pt films that are formed by ALD have been measured at 50–320 K. The MS model cannot be simply applied to predict the electrical conductivity of the Pt film since the density of the film is thickness dependent at the initial stage of ALD growth. The deviation between calculated L and L_0 is mainly due to phonon conduction. The increased contribution of impurity scattering explains the temperature dependence observed in electrical and thermal conductivities of the ALD Pt films.

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REFERENCES

- (1) Cui, Y.; Lieber, C. M. *Science* **2001**, 291, 851–853.
- (2) Tans, S. J.; Verschuere, A. R. M.; Dekker, C. *Nature* **1998**, 393, 49–52.
- (3) Pop, E.; Sinha, S.; Goodson, K. E. *Proc. IEEE* **2006**, 94, 1587–1601.
- (4) Lee, J.; Li, Z.; Reifenberg, J. P.; Lee, S.; Sinclair, R.; Asheghi, M.; Goodson, K. E. *J. Appl. Phys.* **2011**, 109, 084902.
- (5) Kittel, C.; McEuen, P. *Introduction to solid state physics*; Wiley: New York, 1986; Vol. 4.
- (6) Stojanovic, N.; Maithripala, D. H. S.; Berg, J. M.; Holtz, M. *Phys. Rev. B* **2010**, 82, 075418.
- (7) Leskelä, M.; Ritala, M. *Thin Solid Films* **2002**, 409, 138–146.
- (8) Ritala, M.; Kukli, K.; Rahtu, A.; Räisänen, P. I.; Leskelä, M.; Sajavaara, T.; Keinonen, J. *Science* **2000**, 288, 319–321.
- (9) Mayer, T. M.; Elam, J. W.; George, S. M.; Kotula, P. G.; Goeke, R. S. *Appl. Phys. Lett.* **2003**, 82, 2883–2885.
- (10) Davidson, B. D.; Seghete, D.; George, S. M.; Bright, V. M. *Sens. Actuators, A* **2009**, 166, 269–276.
- (11) Yoneoka, S.; Liger, M.; Yama, G.; Schuster, R.; Purkl, F.; Provine, J.; Prinz, F. B.; Howe, R. T.; Kenny, T. W. *IEEE Int. Conf. Micro Electro Mech. Syst., Tech. Dig.*, 24th **2011**, 676–679.
- (12) Dillon, A. C.; Ott, A. W.; Way, J. D.; George, S. M. *Surf. Sci.* **1995**, 322, 230–242.
- (13) Groner, M. D.; Fabreguette, F. H.; Elam, J. W.; George, S. M. *Chem. Mater.* **2004**, 16, 639–645.
- (14) Aaltonen, T.; Ritala, M.; Sajavaara, T.; Keinonen, J.; Leskelä, M. *Chem. Mater.* **2003**, 15, 1924–1928.
- (15) Lu, L.; Yi, W.; Zhang, D. L. *Rev. Sci. Instrum.* **2001**, 72, 2996–3003.
- (16) Stark, I.; Stordeur, M.; Syrowatka, F. *Thin Solid Films* **1993**, 226, 185–190.
- (17) Costescu, R. M.; Cahill, D. G.; Fabreguette, F. H.; Sechrist, Z. A.; George, S. M. *Science* **2004**, 303, 989–990.

- (18) Zhang, X.; Xie, H.; Fujii, M.; Ago, H.; Takahashi, K.; Ikuta, T.; Abe, H.; Shimizu, T. *Appl. Phys. Lett.* **2005**, *86*, 171912.
- (19) Zhang, Q. G.; Zhang, X.; Cao, B. Y.; Fujii, M.; Takahashi, K.; Ikuta, T. *Appl. Phys. Lett.* **2006**, *89*, 114102.
- (20) Rosezin, R.; Nauenheim, C.; Trellenkamp, S.; Kügeler, C.; Waser, R. *Microelectron. Eng.* **2009**, *86*, 2275–2278.
- (21) Vancea, J.; Hoffmann, H.; Kastner, K. *Thin Solid Films* **1984**, *121*, 201–216.
- (22) Fuchs, K. *Proc. Cambridge Philos. Soc.* **1938**, *34*, 100–108.
- (23) Sondheimer, E. H. *Adv. Phys.* **2001**, *50*, 499–537.
- (24) Mayadas, A. F.; Shatzkes, M.; Janak, J. F. *Appl. Phys. Lett.* **1969**, *14*, 345–347.
- (25) Mayadas, A. F.; Shatzkes, M. *Phys. Rev. B* **1970**, *1*, 1382–1389.
- (26) Zhang, Q. G.; Cao, B. Y.; Zhang, X.; Fujii, M.; Takahashi, K. *Phys. Rev. B* **2006**, *74*, 134109.
- (27) Lim, J. W.; Isshiki, M. *J. Appl. Phys.* **2006**, *99*, 094909.
- (28) Jiang, X.; Huang, H.; Prinz, F. B.; Bent, S. F. *Chem. Mater.* **2008**, *20*, 3897–3905.
- (29) Puurunen, R. L. *J. Appl. Phys.* **2005**, *97*, 121301.
- (30) White, G. K.; Woods, S. B. *Can. J. Phys.* **1955**, *33*, 58–73.
- (31) Heino, P.; Ristolainen, E. *Microelectron. J.* **2003**, *34*, 773–777.
- (32) Ou, M. N.; Yang, T. J.; Harutyunyan, S. R.; Chen, Y. Y.; Chen, C. D.; Lai, S. J. *Appl. Phys. Lett.* **2008**, *92*, 063101.