ATOMIC LAYER DEPOSITED PLATINUM AS A SENSOR MATERIAL: UNIFORMITY, 1/F NOISE, AND YOUNG'S MODULUS

T.S. English^{1,}, F. Purkl^{2,3}, A. Daus², J. Provine¹, Y. Won¹, G. Yama², A. Feyh²,
G. O'Brien², K.E. Goodson¹, O. Ambacher³, and T.W. Kenny¹*

¹Stanford University, Stanford, California, USA

²Robert Bosch RTC, Palo Alto, California, USA

³University of Freiburg, Freiburg, Germany

ABSTRACT

This paper examines previously unmeasured properties of atomic layer deposited Pt films relevant to sensor design, including wafer-scale uniformity, 1/f noise, Young's modulus, and the dependence of all these parameters on ALD processing. We observe an increase in the 1/f noise Hooke parameter of nearly two orders of magnitude with decreasing thickness, which introduces constraints on the design of ALD Pt sensors with low noise requirements. Additionally, we measure the variation in wafer-scale electrical uniformity and Young's modulus with thickness, highlighting tradeoffs associated with integrating ALD Pt films into wafer-scale processing to achieve freestanding structures with high yield.

INTRODUCTION

Atomic layer deposition (ALD) provides several advantages in the fabrication of thin films, including the ability to deposit highly conformal and dense polycrystalline metals with low impurity concentrations and digital thickness control between the limits of nucleation and ~ 50 nm in thickness [1]. The upper thickness limit is generally determined by practical considerations, such as precursor cost and deposition time. Within this regime, ALD provides a unique opportunity to engineer and broadly tune material properties at the atomic scale.

Plasma-enhanced atomic layer deposition (PEALD) of Pt is of particular interest in sensor applications for several reasons. First, Pt has desirable thermistor properties, including a high temperature coefficient of resistance (TCR), low 1/f noise, and corrosion resistance [2]. These qualities have led to the adoption of resistive platinum thermometers in numerous sensor applications spanning a wide range of temperatures and operating environments. Second, the ratio of heat capacity (C_{th}) to thermal conductance (G_{th}) in freestanding PEALD Pt films can be tuned due to increased scattering of energy carriers contributing to G_{th} on grain boundaries and surfaces [3], providing an avenue to engineer small thermal time constants ($\tau_{th} = C_{th}/G_{th}$) below 100 μ s. This enables higher bandwidth sensors in applications which were formerly limited by the thermistor thermal time constant. Third, by using plasma-enhanced recipes and seed layers optimized for nucleation, sub-20 nm Pt films can be deposited whose Young's modulus and density are within 15 and 5 percent of bulk values, respectively. These robust mechanical properties allow for freestanding structures with aspect ratios as large as 10,000:1 to be integrated with traditional batch wafer-scale processing [4].

In recent years, we've reported the fabrication of uncooled infrared detectors (bolometers) whose performance benefits from these unique characteristics of atomic layer deposited Pt [4,5]. However, practical questions remain, including, at what lower limit of Pt thickness do these beneficial characteristics begin to degrade? In the regime above ~ 12 nm, sheet resistance of PEALD Pt films scale linearly with film thickness. However, below this thickness, sheet resistance scales non-linearly in the regime where nucleation effects and Volmer-Weber style growth occur before a

continuous and fully dense polycrystalline film is formed. Nucleation strongly influences the evolution of film properties beyond the formation of a conducting film. As a result, many properties of Pt pertinent to sensor design evolve gradually with a dependence on the film nucleation history. This introduces practical design tradeoffs to ensure not only that material properties are reliably obtained, but also that the films have both sufficient mechanical robustness to survive processing and uniformity to meet design specifications with high yield.

To obtain a more complete understanding of PEALD Pt as a sensor material in the sub-20 nm regime, we characterize the evolution of wafer-scale uniformity, 1/f noise, and Young's modulus through the transition from contiguous nucleation islands to continuous and dense films.

FABRICATION

300, 200, 150, 125, and 100 cycle PEALD Pt films are co-deposited in a Cambridge Nanotech Fiji reactor onto oxidized 4-inch silicon wafers coated with 5 nm PEALD Al_2O_3 and die containing polysilicon cantilever arrays. Following Pt deposition, the sheet resistance of each ALD film is measured at 49 equally spaced locations using an automated wafer probing station. Measurements are performed using a blunt ruthenium tipped probe and care is taken to ensure that the measurement locations do not coincide with the regions of Pt subsequently patterned to form 1/f noise test structures. Center tapped 4-point probe tests structures (also referred to as 5-point probes) are patterned by ion milling to form matched resistors for insertion into the lower half of a Wheatstone bridge. A scanning electron microscopy (SEM) image of a test structure is shown in Fig. 1. Each die contains arrays of 5-point probe test structures with nominal resistances spanning from $\sim 100 \Omega$ to more than 100k Ω . Following ion milling, 10 nm of Cr and 100 nm of Pt are evaporated to form an adhesion layer and bond pads for electrical contact.

Figure 1: SEM of a 5-point probe 1/f noise test structure.

The Young's modulus is determined by measuring the resonant frequency shift of cantilevers before and after conformal ALD coating using a laser doppler vibrometer. The details of the experimental setup [6] and analysis are outlined elsewhere [7].

Materials Characterization

Each film is characterized using high-resolution transmission electron microscopy (TEM) in both cross-section and plan-view configurations. Figure 2 shows TEM characterization of a subset of PEALD Pt films which span thicknesses > 15 nm (continuous & fully dense) down to < 7 nm (discontinuous) which exhibit Volmer-Weber island growth (Figures 1a,b). A subset of thinner films are characterized using Rutherford backscattering spectrometry (RBS) to provide complementary information to deconvolve thickness, density, and roughness in order to normalize the thickness of discontinuous films to an equivalent thickness at bulk density. This facilitates the comparison of $1/f$ noise in both continuous and discontinuous films using Hooge's empirical formulation, which depends upon the number of charge carriers and was originally intended to describe homogenous films. It is otherwise challenging to independently quantify the thickness, density, and roughness of such films because TEM characterization is strongly influenced by sample preparation and imaging conditions. Specifically, contrast from transmission through multiple grains of a discontinuous film in cross-section can cause films to appear thicker and/or denser than they truly are.

Figure 2: Transmission electron microscopy characterization of a subset of PEALD Pt films showing (c) fully dense and (a,b) non-dense films.

1/F NOISE

Theory

While the origins of $1/f$ noise continue to be debated to this day, there is broad experimental evidence and consensus that $1/f$ noise in metals originates from defects and therefore serves as a metric for the quality of a metal film [8]. The following empirical description of $1/f$ noise was postulated by Hooge

$$S_v(f) = \frac{\gamma V^2}{f^{\alpha} N} \quad (1)$$

where S_v is the power spectral density (PSD) in units of V^2/Hz , N is the number of charge carriers, V is the bias across the sample, γ is an empirical noise parameter (Hooge constant), f is frequency, and $\alpha \approx 1$. The PSD dependence on the number of charge carriers suggests that $1/f$ noise originates from a bulk or volumetric effect, and furthermore, that $1/f$ noise increases with decreasing film thickness. This has motivated a great number of experimental studies with the objective of measuring $1/f$ noise in thin films common in micro- and nanofabrication [9]. However, the limited accuracy of experiments and control in fabrication has precluded systematic studies of $1/f$ noise in polycrystalline metals deposited on substrates where the effects of nucleation on $1/f$ noise can be measured. Furthermore, in the case of Pt, we might expect significant deviations in $1/f$ noise behavior during Volmer-Weber nucleation due to the accompanying transformation of grain structure, defect densities, and electron scattering dynamics.

We have addressed the former limitations by fabricating ALD Pt test structures optimized for $1/f$ noise measurements [10] and by extending recent advances in the design of noise spectroscopy experiments utilizing digital signal processing to remove errors which typically plague the measurement and interpretation of $1/f$ noise measurements in low-noise materials such as Pt [11,12].

Experimental Setup

Direct current (DC) measurements are challenging to apply to low-noise samples due to the $1/f$ noise within the first preamplifier stage itself. Additionally, low frequency temperature and biasing drifts can corrupt the $1/f$ noise measurements and prevent accurate determination of the experimental noise floor. Surrounding this challenge is the question of whether one is measuring the noise of the actual DUT, as desired, or the $1/f$ noise of the instrumentation in the signal path and interference from other sources. Alternating current (AC) measurements with a Wheatstone bridge provide a means of modulating the $1/f$ voltage fluctuations as noise sidebands at a frequency chosen such that the preamplifier $1/f$ noise is negligible (i.e., typically $250 \text{ Hz} < f < 1000 \text{ Hz}$). A dual channel commercial DSP lock-in amplifier (Zurich Instruments) is used to provide synchronous modulation of the $1/f$ noise, phase-sensitive detection, and direct digital acquisition of the voltage time series at the output filter of the lock-in. Furthermore, phase sensitive detection allows the background experimental noise floor to be measured simultaneously during data acquisition. By subtracting the in-phase signal ($1/f$ noise + background) from the out-of-phase signal (background), a differential measurement is made in the frequency domain, providing further rejection of external noise sources along with a direct assessment of the noise floor of the experiment. Figure 3 shows a schematic highlighting key features of the experimental setup. A typical set of PSD measurements from a 125 cycle PEALD Pt film are shown in Fig. 4 for several applied voltages and a summary of $1/f$ noise measurements performed at 40°C appear in Table I.

Figure 3: Overview of the $1/f$ noise experimental setup. The front end signal path is reconfigurable to allow for optimal matching to the sample impedance using a step up transformer pre-amplifier (no power gain) and high input impedance, low-noise differential JFET pre-amplifier. Conducting thermal paint is used to attach die to leadless chip carriers which are mounted to a copper liquid heat exchanger using a zero insertion force holder. A temperature controlled thermal bath provides long-term temperature stability without the noise of active temperature control elements.

Figure 4: Noise power spectral density of a 125 cycle Pt film measured at several voltages.

Table 1: Summary of measured $1/f$ noise properties.

PEALD Pt Cycles	100	125	150	200	300
Thickness (nm) @ bulk density	4.6	6.6	8	10.7	16
$1/f$ Hooge Parameter	1E-2	1.5E-3	2.8E-4	2.4E-4	2.4E-4
$1/f$ exponent	1.13	1.16	1.16	1.15	1.16

After acquiring the voltage fluctuation time series directly from the lock-in, all subsequent data reduction is performed in the digital domain using digital signal processing. The voltage time series output at the lock-in is oversampled and decimated by a factor of 32 using finite impulse response filters to achieve fast roll off with a narrow transition band. This reduces the equivalent noise bandwidth while improving rejection of out-of-band noise.

EXPERIMENTAL RESULTS

The scaling of resistivity, TCR, $1/f$ noise Hooge parameter, and Young's modulus with number of ALD cycles is shown in Fig. 5. We observe an increase in the $1/f$ noise Hooge parameter of nearly two orders of magnitude below 10 nm as the film approaches nucleation. However, above this transition, PEALD Pt films display low $1/f$ noise for which Pt is known. In thermistor applications, the ratio of TCR to $1/f$ noise constant is a metric of interest that relates the sensitivity (thermal to electrical transduction) with the noise performance of the thermistor itself. In this context, it is interesting to note that the overall thermistor performance is reduced, not only by increasing $1/f$ noise below 10 nm (150 cycles), but also by a reduction in the magnitude of the transduced signal due to reduced TCR. An average Young's modulus of 146 GPa was measured for continuous films in the 10-16 nm regime (figure 5d), between 85-90% of the bulk Pt value. Collectively, the trends in figures 5a-d highlight two important regimes surrounding the formation of continuous and dense films, below which the desirable properties of PEALD Pt degrade.

Figure 5: Measured resistivity with error bars reflecting uniformity, TCR, $1/f$ noise Hooge parameter, and Young's modulus as a function of PEALD Pt thickness normalized to bulk density.

Increasing non-uniformity with fewer ALD cycles may lead to portions of a wafer containing severely degraded thermistor properties (i.e., higher $1/f$ noise, lower TCR) and heightened sensitivity to processing conditions. While this presents challenges in fabricating devices close to the transition point, it also presents an opportunity to develop tuned recipes which may improve nucleation and wafer-scale uniformity. For example, three PEALD Pt recipe variations are evaluated to improve uniformity and quality of 100 cycle films by altering carrier gas dynamics during deposition. Sheet resistance was measured at 225 points per wafer and binned to form the histograms shown in Fig. 6. We observe that recipes tuned for the Pt precursor chemistry dynamics can reduce sheet resistance by nearly 35% due to improved grain nucleation and morphology while reducing the non-uniformity (standard deviation/average) to between 1 and 2%. An assessment of film thickness and density by TEM and RBS measurements indicate a corresponding reduction in resistivity. Figure 7 shows the improved spatial distribution of non-uniformity achieved with a tuned recipe.

Figure 6: Sheet resistance histograms constructed from 225 wafer-scale measurements of 100 cycle films demonstrating an ability to tune electrical properties and uniformity via ALD recipe. Thickness & density were independently measured by TEM and Rutherford Backscattering spectrometry.

Figure 7: 4" wafer sheet resistance maps plotted with a constant color scale centered on the mean sheet resistance of each wafer.

CONCLUSIONS

At the lower thickness limit approaching nucleation, the ideal thermistor properties of PEALD Pt are found to degrade due to increasing $1/f$ noise and a corresponding reduction in TCR. This may drive tradeoffs and practical lower limits to thickness in the design of ultrathin PEALD Pt sensors. In contrast, we observe that PEALD Pt films retain their excellent thermistor and mechanical properties with increasing thickness above a transition point corresponding to the formation of dense and continuous films with a mature grain structure. The interplay between material properties, ALD recipes, and wafer-scale uniformity highlight the challenges of using PEALD Pt as a sensor material near the observed transition. Future work in this area includes the development of tuned ALD recipes targeting improved electrical, thermal, and

mechanical properties of ALD Pt films for emerging sensor applications.

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CONTACT

*T.S. English; englight@stanford.edu