Piezoresistive Pens for Dip-Pen Nanolithography

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ABSTRACT

The conventional approach to measurement of the deflection of microfabricated cantilevers centers on the use of an optical lever. The use of optical lever technology increases the size, complexity, and cost of systems using microfabricated cantilevers. Occasionally, piezoresistors have been used to sense deflection. But, for atomic force microscope applications in particular, topographical sensitivity has demanded the higher sensitivity of the optical lever. For dip-pen nanolithography (DPN) microfabricated cantilevers do not require the same degree of deflection sensitivity. So, for these applications, piezoresistors can be used to sense deflection. In this work, we present a novel approach to an integrated DPN pen. Piezoresistive silicon stress sensors are integrated into a silicon nitride cantilever. The device design, process design, and fabrication methods for building these sensors, and sensor-actuators, are demonstrated. Integration of heaters, along with the piezoresistors, is also demonstrated.

Keywords: dip-pen nanolithography, microfabricated cantilevers, piezoresistive sensing, biomolecular printing, AFM

1. INTRODUCTION

DPN (dip-pen nanolithography) has found wide-ranging applications, from electronics to materials science to biology, at size scales from at small as 10 nm for dry ink printing, and several um for wet ink printing. Typically, DPN requires one pen for writing, and another for reading (x,y) position, and reading what has been written. Also typically, optical lever means have been employed to determine vertical position for the reader pen.

In this work, we present a novel approach to an integrated DPN pen. Piezoresistive silicon stress sensors are integrated into a silicon nitride cantilever. Connecting two such sensors on the cantilever, and two reference sensors off the cantilever (but in close proximity, due to noise considerations), into a Wheatstone bridge, provides electrical readout of vertical pen displacement. For some of the pens, thermal actuators are also integrated, allowing active pen control plus electrical vertical pen position readout. We will demonstrate the fabrication method for these devices.

Our approach places electrically conductive piezoresistors onto electrically insulating cantilevers, which eliminates the electrical leakage associated with piezoresistors embedded in semiconducting or conducting cantilevers, thereby improving the noise figure of the sensors. In addition, silicon nitride cantilevers are less brittle than single crystal silicon cantilevers. Also, silicon nitride tips are much less susceptible to fracture than single crystal silicon, and therefore longer-lasting.

2. PROCESS DESIGN

Figure 1 shows a 3D schematic of an integrated DPN piezo-pen. It is a standard silicon nitride AFM-style pen[1], with several enhancements. A previous enhancement addressed the desire for pen actuation, which is realized using a thermal actuator/resistor: changes in the temperature of the thin metal resistor film cause changes in the overall stress in the AFM cantilever, resulting in bending[2]. The enhancement in this work is to add a pair of piezoresistive stress sensors, not to an electrically-conductive cantilever[3-5], but to an electrically-insulating cantilever. Piezoresistors embedded in semiconductors tend to leak electrically, due to enhanced electric fields at curved corners, and the relationship between diode leakage currents and electric field.

These sensors replace the standard optical lever approach to vertical position measurement[6]. They are incorporated into a Wheatstone bridge, whose voltage output becomes a function of the amount of bending in the cantilever.

The silicon nitride pen tip can be either blunt, or with a radius of 5 nm. The silicon nitride is typically 0.6 um thick, and is silicon-rich in nature, so that the stresses in the thin silicon nitride film are at once low, and controllable through silicon nitride the deposition process. Residual stresses in our cantilevers are typically less than 100 MPa.

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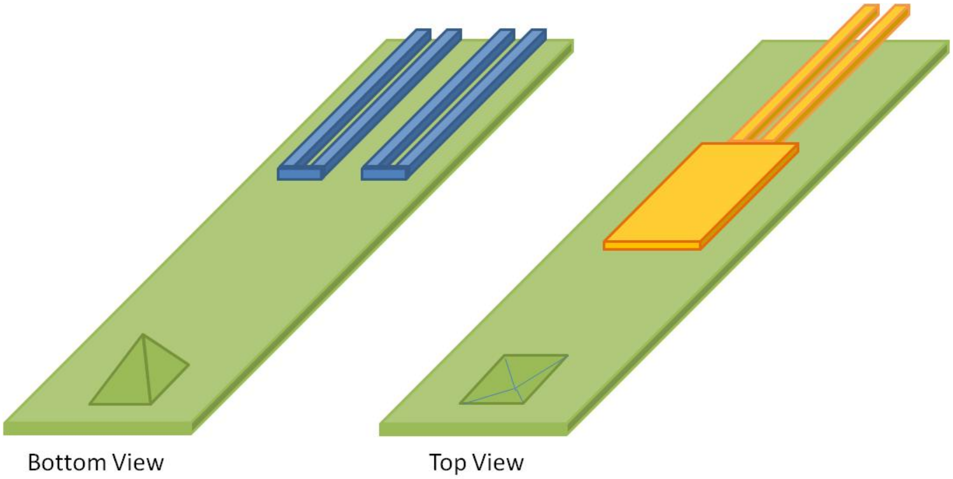
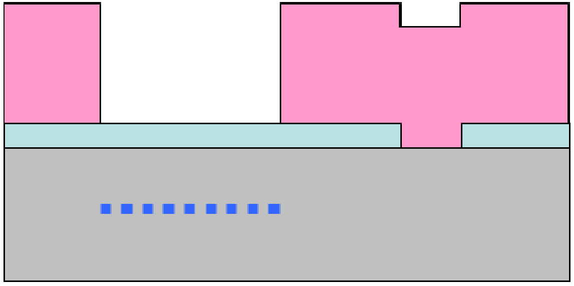


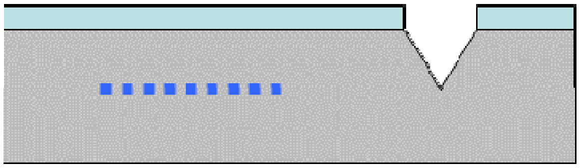
Figure 1: 3D schematic of standard AFM pen, with integrated thermal actuator, and piezo-resistor for either vertical or torsional position sensing.

Figure 2 shows a schematic of the process flow to realize the piezo-pens. The process begins in Step 1 with growth of a thermal oxide, followed by opening the oxide where the pen tips will be. Step 2 masks the wafer, with openings for a high energy, high dose Boron implant, which forms the piezoresistor. Step 3 is a KOH etch, using the oxide mask, to form the pyramidal molds for the pen tips. Step 4 strips the first oxide, and regrows an oxide: the re-grown oxide forms the mold for a very sharp (5 nm radius) tip for the pen, which is especially important for deposition of diffusive (instead of liquid) inks. Note that the oxidation in Step 4 broadens the vertical range of the piezoresistor implant. Step 5 removes the sharpen oxide except in the vicinity of the tip. Step 6 casts the silicon nitride onto the mold wafer. Low-stress, silicon-rich nitride is used, in the conventional manner for MEMS devices. Step 7 is a high temperature anneal in an Argon ambient, whose purpose is to move the Boron dopant so that a high concentration is found directly against the silicon/silicon nitride interface. Step 8 shows the results after two lithography steps: the first opens holes in the silicon nitride in order to form electrical contacts to the piezoresistors; the second is a patterned photoresist used to deposit a TiPtAu metallization, for carrying signals to and from the piezoresistors, and the thermal actuators. After this step, a wafer level, gold-gold thermo-compression bond is formed between the pen wafer, and a handle wafer. Step 9 shows the final cross-section schematic, after the bonded wafer pair is immersed in TMAH, until all the silicon on the pen wafer is removed, save for the heavily Boron doped piezoresistors. Note that most of the silicon handle wafer is protected by silicon nitride during the TMAH etch release process.

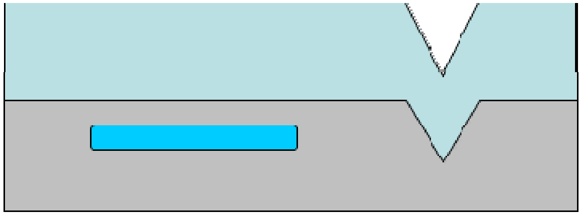
1. Tip definition: grow 100 nm oxide; pattern



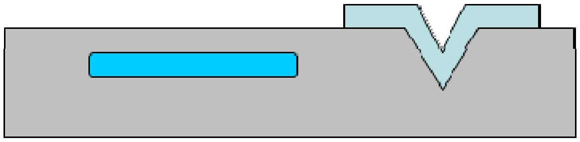
2. Piezoresistor implant: 5E16 cm^{-2}, 150 keV, B11



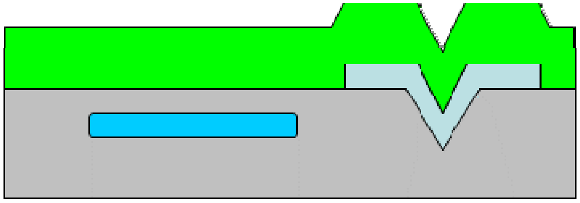
3. Tip etch



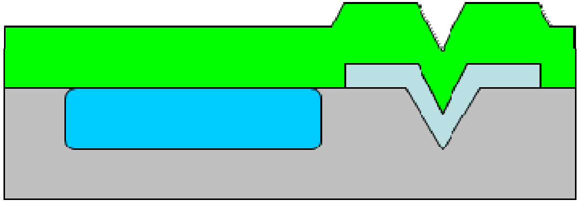
4. Strip oxide; grow Tip Sharpen oxide



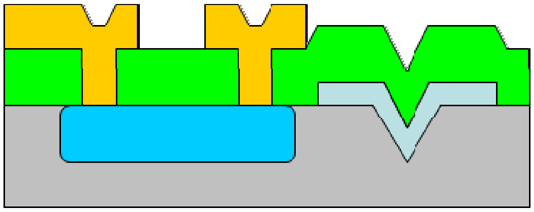
5. Etch Tip Sharpen oxide; remove photoresist



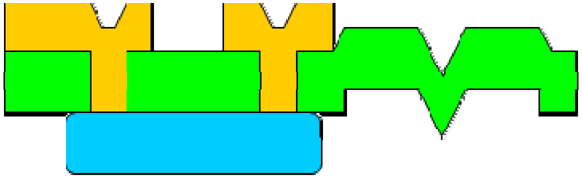
6. Deposit silicon nitride



7. Piezoresistor anneal: 1000 ºC Argon, 3 hrs



8. Cantilever and contact etch; TiPtAu deposition and lift-off



9. Wafer bond; TMAH release etch; final oxide etch

Figure 2: Schematic process flow for piezo-pen manufacture. A step not shown, between Steps 8 and 9, involves gold-gold thermo-compression bonding of the pen wafer to a metalized handle wafer.

A central innovation in our approach is the attachment of the conductive piezoresistors to the underside of the cantilever, with electrical vias through the cantilever body to connect to the thin film metal wires which eventually connect externally to sensing electronics (amplifiers) through conventional wire bonds. Use of the process simulator FLOOPS[7] was made, in order to quantify the implant energy and dose, and drive-in time and temperature, which assure the Boron dopant concentration exceeds roughly 3E20 cm-3: the threshold required to ensure minimal etching in the TMAH solution, used to release the cantilevers mechanically[8].

Figure 3 shows the key to this innovation: how to attach an electrically conductive piezoresistor to an electrically insulating silicon nitride cantilever? As mentioned earlier, to add the piezoresistor, ion implantation is used place a heavy concentration of Boron below the silicon surface. Subsequently, after the silicon nitride deposition, the implanted dopant atoms experience a thermal drive-in sequence, which moves the high concentration of Boron into contact with the silicon nitride. When the cantilever is finally released, via a TMAH silicon etch, the high concentration of the piezoresistor ensures its etch resistance against the TMAH. Figure 3, therefore, shows the evolution of the implanted boron during processing.

Note that a depth of 0 um defines the original silicon surface, before the second oxidation. The second oxidation, however, consumes a little more than 0.2 um of silicon. This consumption is reflected in the plot of concentration vs. depth: the Boron dopant concentration begin at a depth of 0.21 um (the sharpening oxide is about 0.5 um thick). The red line in the graph indicates the concentration profile chosen for our process. A 3 hr anneal balanced process time against the requirement to achieve as high a concentration of Boron as possible at the silicon/silicon nitride interface (which is also at 0.21 um of depth). The concentration needed to be high, in order to allow the piezoresistors to survive the TMAH release etch at the end of the overall process.

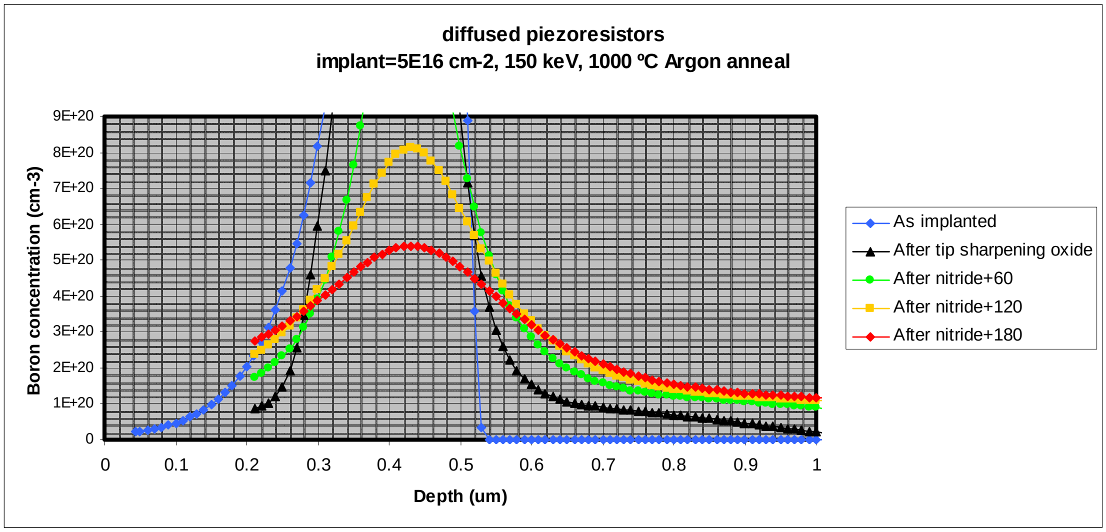


Figure 3: Simulation of high-dose, high-energy Boron implant, used to create the piezoresistors. The effect of subsequent process steps on the evolution of the Boron doping profile is shown. In particular, three different anneal times are simulated, in order to arrive at an anneal time which preserves the piezoresistor resistance to KOH and TMAH etching.

Figure 4 shows the top-down view of several piezo-pen designs. In these design view, cyan or turquoise is the silicon nitride layer, solid red is the pen tip, white is the contact, purple is the Boron implant, and gold and grey are the metal layers associated with, respectively, the pen wafer and the handle wafer. The grey and gold layers are bonded together physically with a gold-gold thermocompression bond, where (in the design) they lie atop each other.

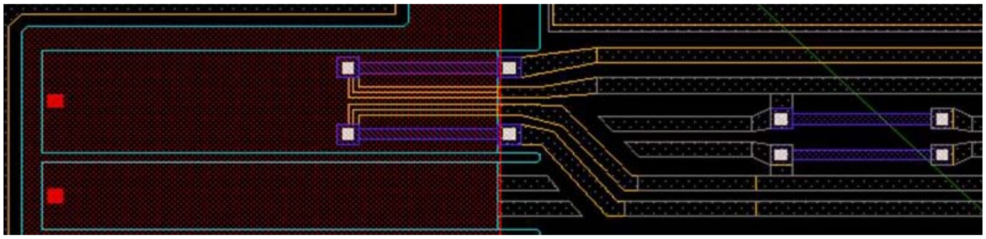
Figure 4a shows a piezoresistor design where the deformable resistors on silicon nitride cantilever are contacted by metal which also is upon the cantilever. (Note that the mechanically fixed resistors, which form the reference portion of the Wheatstone bridge sensor configuration, are shown at the right.)

Figure 4b shows a similar design, except here all metal is kept off of the cantilever, so that the dominant mechanical response of the sensor is due to the intrinsic properties of the silicon nitride, with only a slight modification due to the presence of the piezoresistors.

Figure 4c shows a cantilever carrying two sets of piezoresistors: one set, near the fixed end of the cantilever, measures longitudinal deflection, and is positioned near the point of maximum longitudinal stress; while the second set, near the free end of the cantilever, measures the torsional deflection. Reference piezoresistors are again evident in the drawing.

Figure 4d shows a cantilever with both a piezoresistive sensor, and a thermal actuator. The gold resistor is attached to a ‘paddle’, which distributes the heat generated by the metal resistor. Note that the piezoresistor lies on the same side as the pen tip, while the thermal actuator lies on the opposite side.

Figure 4e shows the design for a complete pen ‘chip’, including both the pen wafer and the handle wafer. On the left are the eight pens in this design. Twenty leads, which can be wire bonded, carry signals to and from the individual pens, whether the signals be related to piezoresistors, or to thermal actuators. Principally, in a linear array of eight pens, the outer pens will be fitted with piezoresistive sensors, while the inner pens are not. This arrangement is intended to allow the outer pens to be used to sense the position (vertical position, as well as level position) of the array. The inner pens are typically then reserved for writing or depositing inks, and not for position sensing.



a)

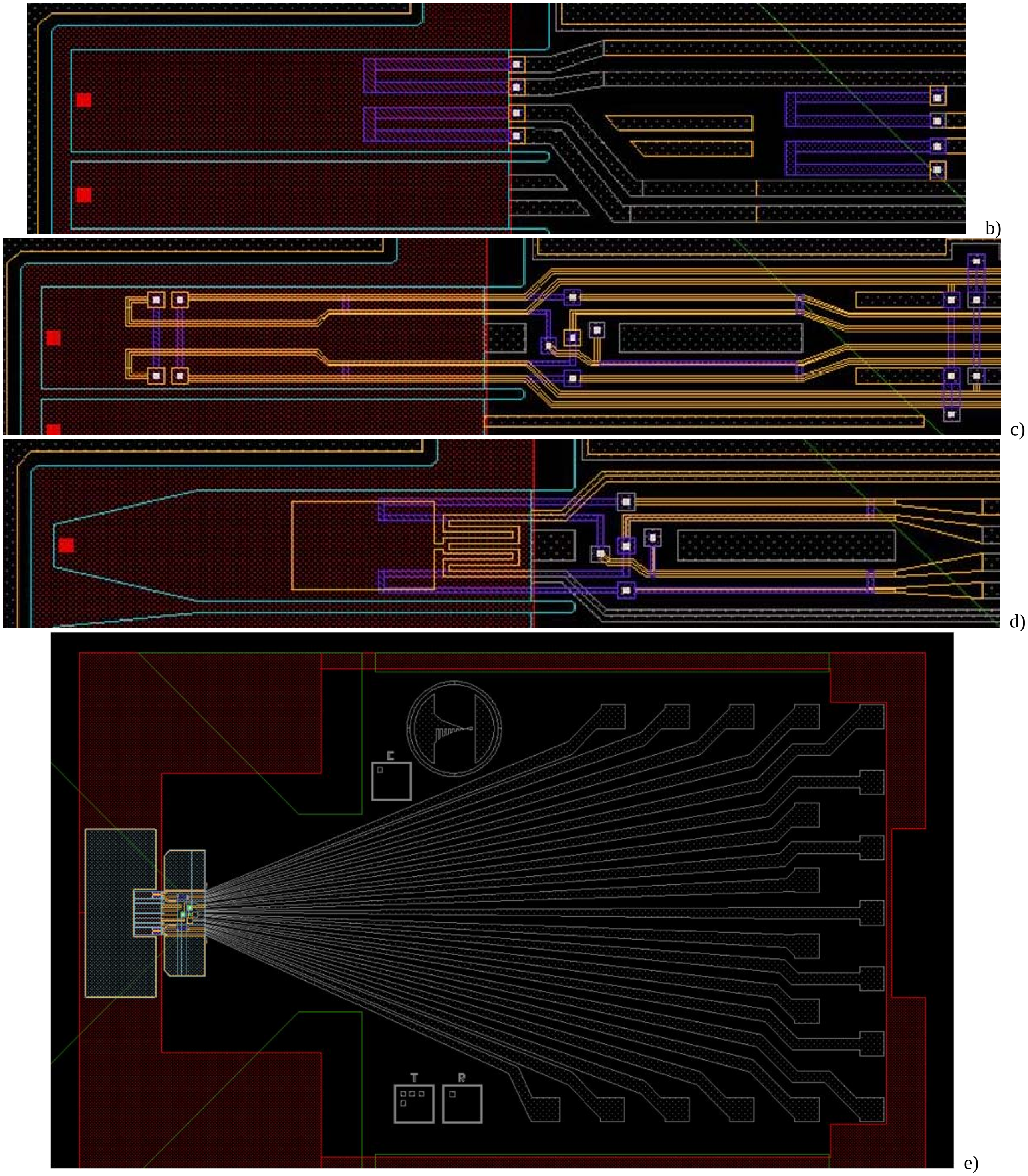


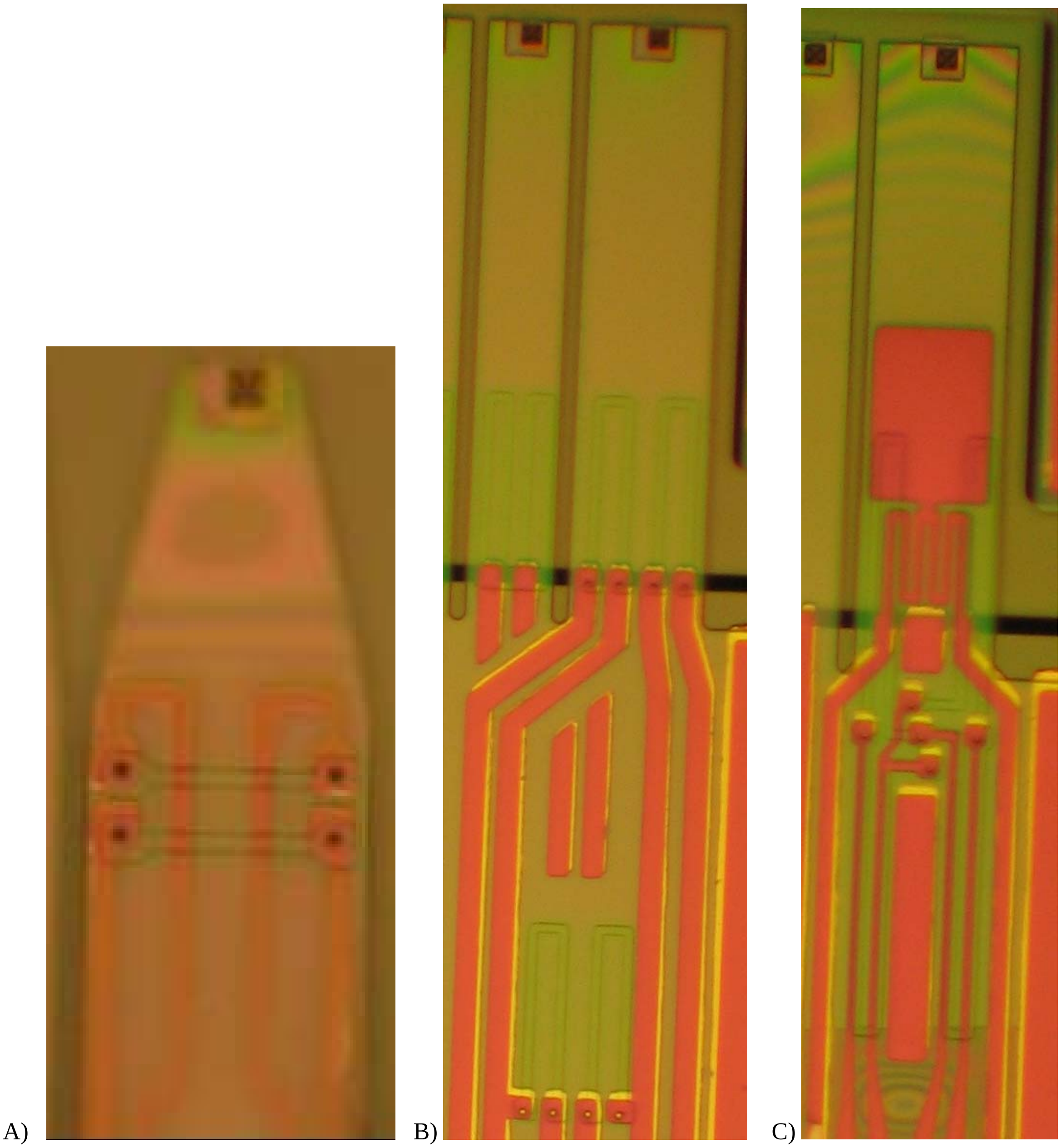
Figure 4: Top-down view of piezo-pen designs: a) conventional, two longitudinal resistors (purple) on cantilever (turquoise), two fixed-mechanical resistors on bond area, the cantilever is 40 um wide and 160 um long; b) out-and-back resistors [contacts off-cantilever]; c) torsional piezoresistors as well as longitudinal piezoresistors; d) out-and-back resistors with integrated heater resistor and diffuser plate; e) overall die size is 5.5 by 3.2 mm.

3. FABRICATION RESULTS

Conventional surface and bulk micromachining methods were combined to achieve the integrated pen structures. Low-stress silicon nitride (silicon-rich) was deposited using LPCVD to a thickness of about 6000 Å.

Fabrication lithography was effected using a Suss MA-6 contact printer. Thermo-compression Au-Au bonding was used to bond the device wafer to a silicon handle wafer, using a Suss wafer bonder. After wafer bonding, the cantilevers are released from the device wafer by removal of all the device wafer silicon using TMAH.

Figure 5 shows some examples of the finished piezo-pens.



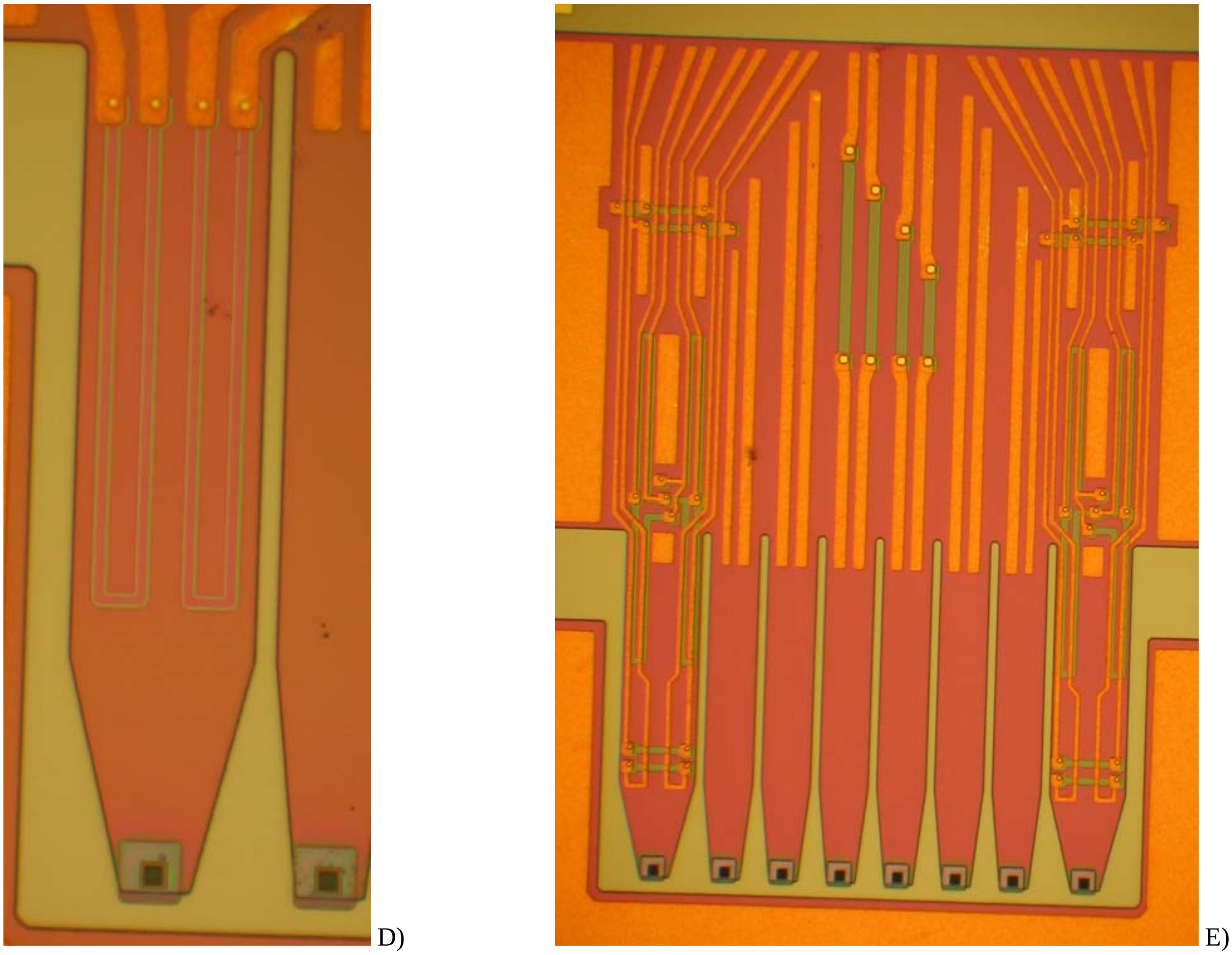


Figure 5: Examples of finished and wafer-bonded piezo-pens: A) torsional piezoresistors; B) out-and-back piezoresistors; C) out-and-back piezoresistors with integrated heater and diffuser; D) long version of the out-and-back piezoresistors; E) a view of an 8-pen array, with six central pens for deposition, and two outer pens for vertical position and leveling purposes, where the outer pens have both longitudinal, out-and-back piezosensors, and torsional piezosensors. In E), the piezoresistors evident in the upper-central portion of the view are used for metrological characterization of the resistance as a function of length. Other metrology structures (such as resistors with varying widths, capacitors, and van der Pauw structures) are incorporated in other die on the wafer. In A), B), and C), the pens are ‘released’: the TMAH etch has already been complete. The interference fringes in C) are a result of the slight bending in the cantilever due to the stress added by the presence of the TiPtAu thermal actuator; the silicon nitride residual stress is low enough, that no similar fringes are evident in A) or B). In D) and E), the pen wafer and the handle wafer have been bonded together using a Suss wafer bonder in thermo-compression bond mode, but the final TMAH release etch has not been performed.

4. DISCUSSION

The most critical step was the etching of the via holes through the silicon nitride, in order to create an ohmic contact between the TiPtAu metallization, and boron-doped piezoresistors. An STS reaction ion etcher, with CHF3+O2 chemistry, was utilized to create these essential vias. Since the thickness of the piezoresistors was only about 0.5 um, care was required: underetching would mean excess silicon nitride in the via, leading to electrical ‘opens’; while overetching would punch through the thickness of the piezoresistor, leading to either ‘opens’, or to contacts with unacceptably high electrical resistance.

5. CONCLUSIONS

We have created integrated AFM-style pens for dip-pen nanolithography applications. The pens integrate thermal actuation and piezoresistive sensing of vertical and torsional position. Uniquely, the devices integrate electrically insulating silicon nitride with electrically conductive silicon piezoresistors. The devices eliminate the optical levers usually found in scanning probe systems for position sensing. The levers are replaced with small-scale electronics, making possible a reduction in size, complexity, and cost for the overall system.

REFERENCES

[1] Salaita, K., Wang, Y., Fragala, J. , Vega, R. A., Liu, C., and Mirkin, C. A., "Massively parallel dip–pen nanolithography with 55,000-pen two-dimensional arrays," Angewandte Chemie 118, 7378–7381 (2006).

[2] Rosner, B., Duenas, T., Banerjee, D., Shile, R., Amro, N., and Rendlen, J., "Functional extensions of Dip Pen Nanolithography^{TM}: active probes and microfluidic ink delivery," Smart Mater. Struct. 15, S124–S130 (2006).

[3] Chui, B. W., "Low-stiffness silicon cantilevers with integrated heaters and piezoresistive sensors for high-density AFM thermomechanical data storage," J. MEMS 7, 69-78 (1998).

[4] Tortonese, M., Barrett, R., and Quate, C., "Atomic resolution with an atomic force microscope using piezoresistive detection," Appl. Phys. Lett. 62, 834–836 (1993).

[5] Goericke, F., Lee, J., and King, W. P., "Microcantilever hotplates with temperature-compensated piezoresistive strain sensors," Sensors and Actuators A143, 181–190 (2008).

[6] Alexander, S., Hellemans, L., Marti, O., Schneir, J., Elings, V., Hansma, P. K., Longmire, M., and Gurley, J., "An atomic-resolution atomic-force microscope implemented using an optical lever," J. Appl. Phys. 65, 164-167 (1989).

[7] Law, M., "FLOOPS Development," <http://www.swamp.tec.ufl.edu/floops.html> (24 August 2012).

[8] Steinsland, E., Nese, M., Hanneborg, A., Bernstein, R. W., Sandmo, H., Kittilsland, G., "Boron etch-stop in TMAH solutions," Sensors and Actuators A54, 728-732 (1996).