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Kamesh V. Gadepally
University of Arkansas at Little Rock

Kevin B. Tennal
University of Arkansas at Little Rock

Roger M. Hawk
University of Arkansas at Little Rock

Al Robles

James A. Gribel

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STUDY OF DEPOSITION METHODS FOR SILICON POWDER

KAMESH V. GADEPALLY, KEVIN B. TENNAL, and ROGER M. HAWK
UALR/GIT, 575 ETAS Building
2801 S. University Avenue
Little Rock, Arkansas 72204

AL ROBLES and JAMES A. GRIBEL
Ameron Powder Coating Company
P.O. Box 9610
Little Rock, Arkansas 72219

ABSTRACT

Silicon powder tends to agglomerate at normal atmospheric conditions and is, hence, difficult to aerosolize. Several methods of aerosolizing silicon powder and finally depositing it on various substrates were investigated. This paper presents the investigated methods of aerosolization. The electrostatic spray coating used in dry paint application was found to be the most suitable. The general merits of this method and its use for silicon powder deposition to form films are discussed.

INTRODUCTION

Thin film deposition of silicon is very important in its applications to solar cells and integrated circuits. The conventional deposition methods are many, but the most prevalent include sputtering, chemical vapor deposition (CVD), and molecular beam epitaxy. The required equipment for these processes is extremely expensive, which affects the finished product cost. Though solid phase deposition and subsequent annealing is used in other industries, it has not been applied to silicon deposition. The technique was successfully applied to silicon film deposits, and could offer significant cost reduction relative to current methodology. Metallurgical powders (Kirk and Othmer, 1981) as well as polymers (Rodriguez, 1967) have been coated on substrates by electrostatic spray application (Miller, 1987). Other methods such as plasma and thermal spraying have been used to deposit ferrites, samarium-cobalt permanent magnets, and ceramic oxides (Kumar, 1988; Kumar and Petrovitch, 1988; Varacalle Jr., *et al.*, 1988). This research focused on using solid phase deposition of silicon powder. Several methods of aerosolizing and depositing the powder were conducted. The most successful results were obtained through electrostatic charging and deposition of silicon on conducting, semiconducting, and insulating substrates. Excellent deposition uniformities have been obtained.

METHODS

DEVELOPMENT OF AN AEROSOL DEPOSITION TECHNIQUE

An appropriate aerosol generation technique has been developed where particles could be either charged or uncharged. Some of the critical considerations for generating the aerosols were to: 1. avoid agglomeration, 2. minimize losses due to deposition on flow tube walls, 3. minimize pickup of contamination, 4. obtain good uniformity of deposition, and 5. obtain repeatability.

Several methods were investigated to aerosolize the silicon powder and deposit it uniformly. These methods utilized fluidized bed, dust feeder, acoustic feeder, and vibrating dispenser techniques among other methods. All these methods have been discussed in detail below. The highest purity of silicon powder available was 99.999% pure silicon as purchased from CERAC Inc. The size analysis was done using a Coulter counter. It was noted that the arithmatic mean diameter was 22.90 micrometers, geometric mean diameter was 17.22 micrometers with a geometric standard deviation of 2.6. Another powder whose average diameter was 5.05 micrometers also was used. The distinction between the two has been made wherever they have been used. A step by step discussion of the methods used to generate the aerosols follows.

FLUIDIZED BED METHOD

As shown in Fig. 1, a fluidized bed was used to generate the aerosol with subsequent deposition on the stages of a 6 stage cascade impactor. This method caused the clumps of particles to form on the bed without aerosolization unless high flow rates (>30 LPM) were used. When very high flow rates were used, the problem of particle bounce was magnified. The cascade impactor is used generally for size distribution analysis. If particles could be size-separated, then substrate deposition of a particular sized particle from a polydispersed aerosol would be made easier by simply adding or subtracting a stage. Only a small quantity of particles entered the cascade impactor because most of the clumps could not be aerosolized at the flow rate compatible with the design requirements of the cascade impactor. Some results that were obtained are described below.

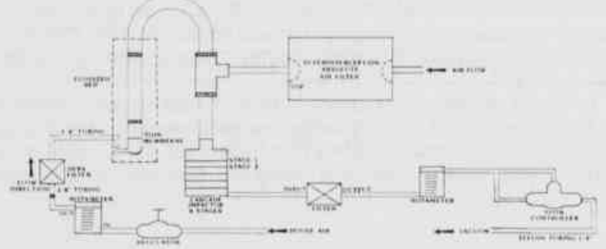


Figure 1. Schematic of the fluidized bed method.

DATA AND OBSERVATIONS

A controlled supply of house air was supplied to a fluidized bed. Silicon dust (−325 mesh or 44 micrometers and smaller) was aerosolized and collected on the 6 stages of our Sierra Series 210 cascade impactor. A cascade impactor filters out particles based on their size by virtue of its filter openings and the flow rate. The filters were weighed before and after collection and the mass percentage was calculated. Typical results are shown in Table 1.

When the flow rate was 14 lpm, the first stage filtered out 13 micrometers and greater particles, the next stage 7.8 micrometers and greater, the third stage filtered 3.1 micrometers and greater, and so on. The last stage filtered out particles 0.63 micrometers and less. When

Table 1. Size analysis on 99.999% pure silicon (−325 mesh).

Flow Rate = 14 lpm

Stage of Cascade Impactor	Cummulative Wt% Collected	Size (um) of Particle
Stage 1	86.61	> 13
Stage 2	91.38	> 7.8
Stage 3	95.83	> 3.1
Stage 4	96.46	> 1.8
Stage 5	96.46	> 1.2
Solid/Stage 6	99.96	> 0.63

The above data are suspect since clumps comprised of finer particles which aerosolized were trapped on the top. However, it provides a rough estimate of the amount of particles in different size ranges.

the flow rate through the cascade impactor was changed, the different stages trapped a different particle size distribution.

The smaller the particle, the better the deposition uniformity. However, particles smaller than 0.63 micrometers are observed from Table 1 to be 0.04%. Thus, they constituted a minor fraction of the total powder that was deposited. One major problem was that of the 85 mg of silicon powder in the fluidized bed, only 3.5 mg was aereosolized even after 30 minutes at an air flow of 14 lpm. The reason was that the silicon powder was very dense and tended to form clumps. This method using a fluidized bed was discontinued.

DUST FEEDER METHOD

A dust feeder replaced the fluidized bed as shown in Fig. 2. A dust feeder has a higher entrance and exit velocity per unit flow rate due to smaller dimensions on the inlet and exit streams. The higher velocity caused the particles to be easily aerosolized. However, 45% by mass of particles deposited on the walls of the flow tube and only 10% of the total powder reached the cascade impactor. The objective was to flow as much powder as possible through the cascade impactor. Since only 10% ever made it to the cascade impactor, this method would not be economically feasible. Data and observations are described below in greater detail.

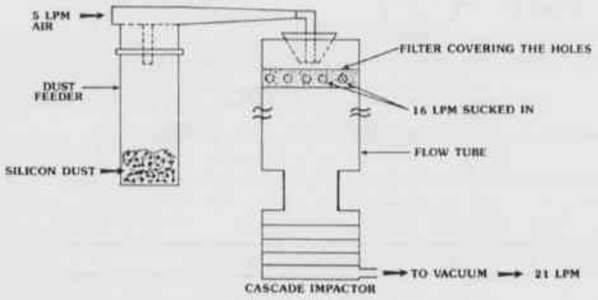


Figure 2. Schematic of the dust feeder method.

DATA AND OBSERVATIONS

Due to the high velocity of entering air, turbulence is created and the lighter particles get fluidized and leave the bottle at high velocity. A large diameter tube with holes on the top covered by a filter was used to blend in additional air to decrease the flow into the cascade impactor as shown in Fig. 2. As the powder was being aerosolized, a lot of it visually was observed to be depositing on the walls of the plastic tubing. The particles tend to develop triboelectric charge and since PVC and plastic are insulating, the particles deposit and stick on the wall. Also, a static guard spray was used to coat the inside of the tube. The result was no different. Approximately 10% collected in the cascade impactor. The spray guard caused the plastic to crack in the area where holes were drilled into the plastic. Initially the flow rate was 14 lpm, but later increased to 21 lpm where more of the dust appeared to aerosolize. A copper tube with holes drilled on the top also was tried to alleviate the triboelectric charging of the silicon. Again, only 10% was collected in the cascade impactor. Table 2 shows the significant results of the experiments and the conclusions reached.

Table 2. Results of the experiments discussed in dust feeder method.

Expt. #	Starting Mass of Silicon (mg)	Mass on the 6th Stage of Cascade Impactor	% Passed Into Cascade Impactor	Vacuum LPM	Flow Rate LPM	Time	Observations and (min)	Flow Tube Material Comments
1	689.7	64.33	9.32	22	16	3	Non-Uniform Deposition	Plastic
2	665.1	70.6	10.61	21.5	16	3	Deposition inside copper tube not clearly observable	Copper
3	920.5	N/A	10.49	22	16	5	Static guard used & uniform deposition of powder obtained on inside walls	Plastic (45% collected in flow tube)

Conclusion 1) particles were charged and particle repulsion caused them to deposit on the wall.

2) when the different stages were observed under an optical microscope many clumps were found on the different stages indicating particle bounce, hence, use of cascade impactor was discontinued.

ACOUSTIC METHOD

In this method, the specific problem of clumping was addressed using an acoustic technique. Figure 3 shows the experimental design. A sierra dichotomous sampler was used to separate the fine from the course particles and direct them into a depositing chamber of a TSI 3100 electrostatic precipitator. The acoustic frequency was 3.5 kHz. A substantial amount of aerosol passed through the sieve, but too much powder placed on the sieve caused it to clog, making this method of no use. The flow through the TSI 3100 electrostatic sampler was maintained at 5 LPM (connected to house vacuum and house air). The particles were deposited on a microscope cover slip and when observed under the optical microscope, their size was 2.5 micrometers or less; this confirmed that dichotomous separation was occurring. Very sparse distribution of particles was observed, however, since very few particles in the aerosol were 2.5 micrometers and less. The major drawback was that the acoustic generator did not deliver a controlled mass flow of particles, but generated spurts. A powder feeder which dropped powder onto the sieve was developed and tried with limited success. Another drawback was the high acoustic levels that were generated, but which were necessary to break any clumps that formed on the sieve. Hearing protection was required and work had to be done in off-hours for the safety of the laboratory workers. This method was not of much use since there remained a problem of control over generation of aeosol. It was decided, therefore, to further characterize the behavior of the powder under the influence of an electric field.

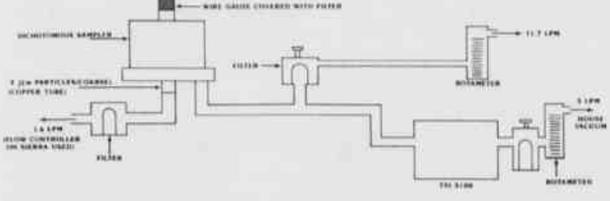


Figure 3. Schematic of the acoustic method.

ELECTRIC FIELD METHOD

Two electrodes were placed into a transparent plastic tube. A dust feeder was used as shown in Fig. 4. It was established from the results in the dust feeder method, Experiment #3, that about 55% of the powder was aerosolized from the bottle and 45% of the total was deposited on the walls of the plastic tube. Hence, the electrodes were placed approximately 5 to 6 cm below the inlet of the dust feeder. One electrode was grounded while a positive charge was placed on the other. The potential was first held at 750 volts DC. Powder deposited on the plates, but not in significant amounts, and the powder flaked easily when deposited on a coverslip and slides. Most of the deposition took place at the bottom end of the electrodes (due to aerodynamic effects). The DC voltage was increased to 3000 volts. This caused the powder to deposit selectively on the positively charged electrode with very little powder depositing on the ground electrode; this showed that the silicon powder was capable of acquiring charge and responding to an electric field. Observations under the Shadow Graph showed fairly thick powder deposition. The particles acquired triboelectric charges.

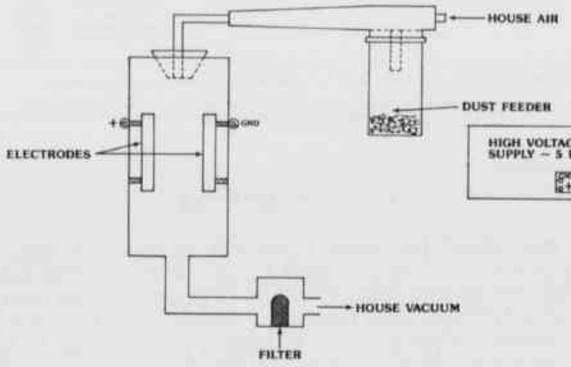


Figure 4. Schematic of the electric field method.

VIBRATING POWDER DISPENSER METHOD

As an extension to the electric field method, a vibrating engraver was used to transfer its vibrations to a powder holder. This is shown in Fig. 5. The base of the powder holder was a 50 micrometer sieve. Particles flowed through the sieve and glass beads were added to break clumps. The voltage did not effect the powder deposition when the aerosol was generated using this method. This was attributed to insufficient charging of the powder.

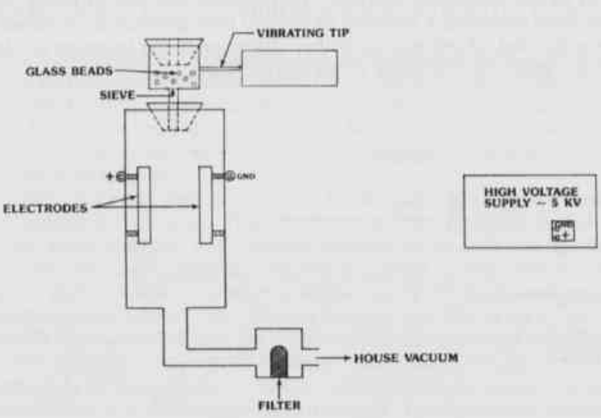


Figure 5. Vibrating powder dispenser method.

Although the powders were not initially charged in both methods, the powder still seemed to acquire charge in the electric field method and not in the vibrating dispenser method. In this method, the particles were not subjected to any bulk attrition, which was the reason the particles were not charged and, therefore, not responding to high electric fields as in electric field method.

As in the other described methods, this method also had its share of problems in generating a uniform powder dust. However, one very important point that was noted between the electric field method and this method was that the silicon particles acquired charge depending on the method used and could retain it until they deposited. This important information was utilized in the next experiment.

ELECTROSTATIC SPRAY DEPOSITION METHOD

Ameron Powder Coating Company in Little Rock is using an electrostatic spraying method to deposit paint pigments on metal substrates that are subsequently heat treated to produce the required finish. A typical powder coating system required the following components: 1. the powder feeder unit, 2. electrostatic powder spray gun, 3. electrostatic power source, and 4. overspray recovery unit.

The powder was supplied by either fluidization or gravity feeding to the spray gun. The flowing gas is generally air which helps in easier transportation and charging. Volume and velocity of the powder flow can be adjusted. The gun used in this research is an external corona charging gun as shown in Fig. 6. The thickness of deposition is controlled by the position of the spray gun, length of spray time, velocity of powder flow, and electrostatic charge level. Silicon powder was introduced into the Ransberg-Gema (Model #706) electrostatic cup gun through a hopper and sprayed. The gun voltages selected ranged from 0 to 100,000 volts DC. Experiments were conducted and the best gun voltage to obtain uniform deposition was found to be 75 kV. Data and details of the above mentioned experiments and technical details on the gun are described below.

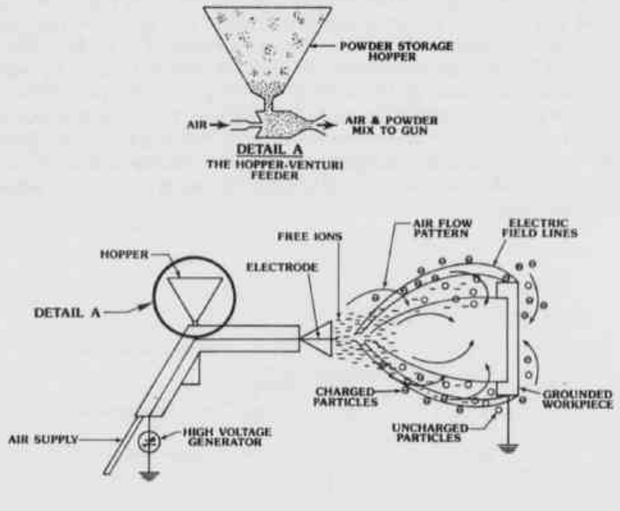
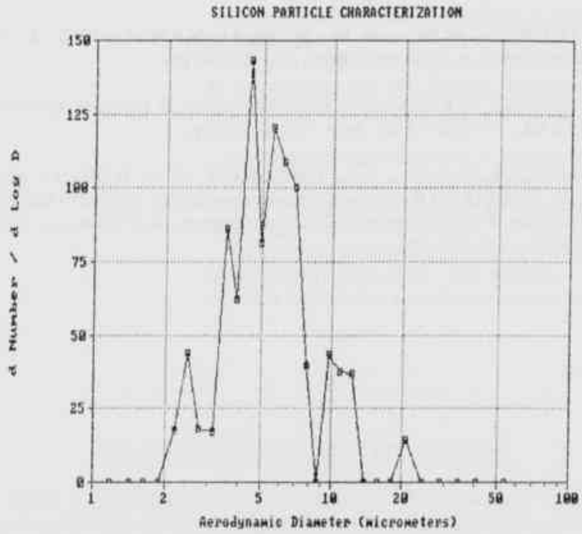


Figure 6. Elecrostatic spray deposition method.

RESULTS AND DISCUSSION

Table 2 shows the results of experiments performed to study the effect of gun voltage on powder deposition and chargeability (coulombs/kilogram). The silicon powder used in this study had a count median aerodynamic diameter of 5.05 micrometers and a purity of 99.999%. The complete size distribution plot obtained by ESPART analysis is shown in Fig. 7. This was the same powder that was obtained after grinding the original 22.90 micrometer powder. Figure 8 shows the results of the effect of gun voltage on the charging ability of the powder. The limiting charge on a spherical particle called the Pauthenier limit (Pauthenier and Moreau-Monot, 1932) is given as follows:



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Mon Feb 12 11:50:18 1990

Sample Time: 579 sec

Count Median Aerodynamic Diameter       = 5.050
Mass Median Aerodynamic Diameter        = 11.219
Count Weighted Geometric Std. Deviation = 1.563
Mass Weighted Geometric Std. Deviation  = 1.680
(Based on data in diameter range 1.00 to 100.00)
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Figure 7. Frequency distribution curve (logarithmic size scale) of ground powder.

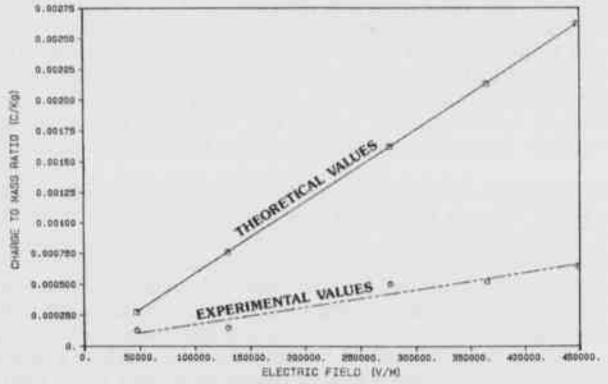

Figure 8. Effect of gun voltage on chargeability of 5.05 μm, 99.999% pure silicon powder.

$$q = 4\pi r^2 \epsilon_o BE$$

where r = particle radius; ϵ_o = permitivity of free space; and E = electric field strength.

$$B = 1 + 2\frac{\epsilon_r - 1}{\epsilon_r + 1}$$

where $B = 2.69$ for silicon powder and ϵ_r = relative permitivity of silicon (11.8). Hence, the limiting charge to mass ratio will be

$$q/M = \frac{3\epsilon_o BE}{rd}$$

where d = density of silicon (2440 kg.m^{-3}). $B = 2.69$ for silicon powder and ϵ_r = relative permitivity of silicon (11.8)

The theoretical values and experimental values are plotted in Fig. 8. The increasing value of electric field indicates increasing gun voltage. Experimental values were lower due to the low charging efficiency of the corona process.

This experiment was done using a fully grounded Nordson aluminum booth as background during spraying. Due to this background, although the gun was set for maximum voltage (100 kV), the voltmeter deflection read 75 kV. The charge acquired per kilogram of particles was determined using a Sheen electrostatic spray diagnostic instrument.

Since success was achieved in depositing these powders and it was established that the silicon powder was charging, it was decided to discontinue development of any of the previously mentioned methods and concentrate research using this method. N and P doped silicon wafers (Monsanto Electronic Materials Corporation-MEMC), single crystal insulating sapphire wafers, and metals were used as substrates. Very good powder coatings were achieved.

TECHNICAL INFORMATION ON RANSBERG GEMA (MODEL #706)

The GEMA 705 (100 kV) powder container: Capacity: 0.8 litres.

TECHNICAL DATA

Pneumatical data

Maximum input pressure:	12 bar
Optimum input pressure:	6 bar
Maximum water vapor content in compressed air:	1.3 g/Nm³
Maximum oil vapor content in compressed air:	0.1 ppm
Maximum compressed air consumption	11.2 Nm³/h

Electrical data

Power supply:
Single-phase AC current, selectable voltages: 100 V (+10%,-15%).
Frequency: 50/60 Hz

Connected loads:	40 VA
Temperature range:	+10°C to +50°C
Nominal input voltage:	10 V eff.
Frequency:	17000 Hz
Nominal output voltage:	100 kV
Nominal output current:	0.07 mA
Maximal output current:	0.15 mA
Polarity:	negative

Lengths of powder hoses and connecting cables

Connecting cable:	5.5 m
Powder hose:	5.8 m

Powder throughput: Maximum powder throughput depends on the length of the powder hose and the type of powder.

CONCLUSION

The electrostatic spray deposition method using the Ransberg Gema (Model #706) gun has been established to be the best method among the methods investigated for uniform silicon deposition. The gun voltage needs to be at least 75 kV. Silicon powder has been coated on conducting, insulating, and semiconducting substrates.

ACKNOWLEDGMENT

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