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- A. "Doping Precipitated Morphology in a-Si:H", E.A. Schiff, P. Persons, H. Fritzsche and V. Akopyan.

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Summary

1. Materials Development. A model for explaining the growth, H incorporation and bandgap data in a-Si deposited from ($\text{SiF}_4 + \text{H}_2$) has been developed. It is proposed that the a-Si films are subjected to reactive ion etching and ion bombardment during growth, which may lead to lower defect densities (and hence lower H content) and microcrystallinity in doped films.

A morphological study of B-doped a-Si:H has also been carried out. It is found that there are certain regions of pressure, temperature and relative B_2H_6 concentrations which lead to agglomerative growth.

2. Material Properties. Study of drift mobility of electrons has continued. We have obtained very high drift mobilities, ($\sim 0.8 \text{ cm}^2/\text{V-sec}$) on thick films ($\sim 3 \mu\text{m}$). Thin films ($\sim 1 \mu\text{m}$) have significantly lower mobilities. It is proposed that this phenomenon is due to the existence of a transition layer between the substrate and high quality a-Si.
3. Device Fabrication. We have continued nip device fabrication in a-Si:H. The following parameters have been obtained individually on cells of 0.24 cm^2 area.

$$J_{\text{SC}} (\text{internal}) = 12 \text{ mA/cm}^2 @ 100 \text{ mW/cm}^2$$

$$V_{\text{OC}} = 820 \text{ mV}$$

$$F = 0.56.$$

4. Device Analysis. Diode factors of 1.2 in light have been achieved, indicating near-perfect diodes.

I. Material Growth

- A. a-Si:H Films. Routine growth of a-Si:H films has continued during this quarter. We have concentrated on growing films for materials measurements (Section II) and devices (Section III).

Our subcontractors at University of Chicago have studied the morphology of a-Si:H films doped with B₂H₆. The major conclusions of their work are:

1. Doping with B can precipitate a grossly inhomogeneous, noncolumnar morphology in critical ranges of B₂H₆/SiH₄ ratio in the gas phase.
2. The inhomogeneous growth may be related to the potential applied to the substrate.
3. The agglomerative morphology may be due to inhomogeneous nucleation, and may be related to precipitation of a-B, since B₂H₆ is known to decompose faster than SiH₄.

The details of their work are in Appendix A.

- B. Growth of Films from SiF₄: The growth of a-Si films from (SiF₄ + H₂) mixtures has been previously shown to yield films with supposedly low density-of-states⁽¹⁾ and high conductivities^(2,3) upon As doping. It has also yielded films with higher bandgap (1.9 - 2.0 eV)⁽⁴⁾ and with low H concentrations (~ 1 - 2%).⁽¹⁾ We have undertaken a study of the growth and electronic properties of these films during this quarter, and propose a model which may explain some of these properties.

During our experiments, we have observed the following phenomena:

1. Growth rate of a-Si films deposited from SiF_4 and H_2 mixtures is very low.
2. Growth rate reduces with increasing substrate temperature, in contrast to the growth of films from SiH_4 .
3. RF (cathodic) films are easier to dope to high conductivity state ($\sim 1 \Omega\text{-cm}^{-1}$) than RF (ground) films.
4. Very high power levels are needed to dope RF (ground) films to the high stage.
5. The bandgap of the RF (ground) films increases as substrate temperature increases, again in direct contrast to the behavior of a-Si:H films deposited from SiH_4 .⁽⁵⁾

Some of our experimental data is shown in Figure 1 - 4. In Figure 1, we show the $\sigma(T)$ curves for two films, one cathodic and one grounded, deposited from identical relative concentrations of SiF_4 , H_2 and AsH_3 . It is obvious that the cathodic film is highly conducting, with $\sigma > 1 (\Omega\text{-cm}^{-1})$ at 300 K, whereas the grounded film behaves very much like a film deposited from SiH_4 alone, with $\sigma \approx 2 \times 10^{-3} (\Omega\text{-cm}^{-1})$. Figure 2 shows the absorption data for the two films of Figure 1. The RF(C) film has a significantly higher E_{gap} ($\sim 1.74 \text{ eV}$) compared to $\sim 1.65 \text{ eV}$ for RF(g) film. The bandgap of the RF(C) film, however, is much smaller than we reported previously⁽⁶⁾. (Compare with Figure 3) We believe this reduction in bandgap is primarily due to our using a significantly purer SiF_4 tank (99.99%) which recently became available from Matheson, Inc. The previous SiF_4 tank from Matheson was relatively impure (99.6%) and contained H_2O and O . It is, of course, well known that addition of O_2 increases the bandgap of a-Si,⁽⁷⁾ and thus, using a purer SiF_4 should reduce the bandgap.

Figure 1

IEC81034

Conductivity of n-type F-etched films

IEC81042

Figure 2

Absorption constants for the two films of Fig. 1

Absorption Constant of a-Si:H and a-Si:F,H

Figure 3

IEC79169

Absorption Constant of a-Si:F,H,O film

In Figure 4, we show the absorption constants for two RF(G) films deposited at 350 and 450°C from identical relative concentrations of SiF_4 , H_2 and PH_3 . The 350°C film had a growth rate of 1.46 Å/s and the 450°C film had a rate of 0.96 Å/sec. The increase in bandgap for the 450°C film compared to the 350°C film is obvious from Figure 4.

We believe that these phenomena, as well as the low concentration of H, can be explained in part by a model that proposes that these films are subjected to reactive ion etching and ion bombardment during growth. (This is somewhat similar to bias sputtering, where the growing film is continually being etched). The net growth rate is determined by a balance between growth and reactive etching of a-Si. It is, of course, well known that SiF_4 can be used to etch Si in a plasma.(8,10)

This model for growth can explain the following phenomena observed in a-Si films deposited from ($\text{SiF}_4 + \text{H}_2$).

1. Necessity for H. If F is reactively etching Si, then it is likely that it etches preferentially the weakly bonded Si atom, namely the disordered or incompletely bonded Si. Thus, it can remove some imperfectly bonded Si, and allow a second chance for a more perfect bond to form. However, some imperfect or dangling Si bonds will remain, and H, being a light atom, will diffuse and attach itself to a broken bond. Thus, H would be absolutely necessary for reducing defect density, but because there are fewer bonds to satisfy, lesser concentrations of H would be needed than for Si deposited from SiH_4 .

Figure 4
Optical Absorption of F-etched a-Si films
on grounded substrates

IEC81093

2. Slow growth rates. Obviously reactive ion etching produces a slower net growth rate. Higher the reactive etching, slower the rate. This can explain why increasing temperature reduces growth rate.
3. Difference between cathodic and grounded films. Cathodic films, being subjected to intense negative voltages, are more likely to be etched and bombarded by ions, and thus become microcrystalline more easily, leading to high σ .(11,12)
4. Bandgap variation. If F is etching weak Si bonds, it is also likely to etch the weak bonds at the top of the valence band, thus driving down the valence band edge, and increasing the bandgap. Thus, increasing etching should be associated with increasing E_g , as observed.
5. High power levels for RF(g) films. At high power levels (several w/cm^2), the plasma voltage is high (+20V) and hence, ionic bombardment of RF(g) films can be more intense, leading to microcrystallinity and high σ .

Thus, our model for the growth of a-Si films from ($\text{SiF}_4 + \text{H}_2$) explains most of the observed phenomena. Whether these films are intrinsically better or worse than a-Si:H deposited from SiH_4 is an unanswered question at this time.

Over the next quarter, we intend to use our recently installed Auger emission spectroscopy apparatus to study the F content of these films, and draw some conclusions about the need for F.

II. Materials Analysis

1. Photoluminescence

We have studied the photoluminescence efficiency of a-Si:H films deposited from SiH₄:H₂ mixtures under three electrical bias conditions. These conditions were: (i) RF (anodic) (ii) DC (cathodic) and (iii) DC (ground). The objective of the experiments was to see if ionic bombardment damages the film.

The results of the experiment are shown in Figure 5. We note that the photoluminescence signals of the RF(A) and DC(G) films are of approximately the same magnitude, but the DC(C) film has a significantly lower signal intensity. This clearly indicates that DC (cathodic) films are damaged by the intense negative voltages (-500 to -1000 V) to which they are subjected. Therefore, we shall not use DC(C) films any more.

2. Mobility Studies

We have continued the study of drift mobility in a-Si:H using the laser time-of-flight technique described in last quarter's progress report. We have done a systematic experiment on studying the drift mobility as a function of the thickness of the a-Si:H film. The results of our experiment are shown in Table I. We note from Table I that the drift mobility increases with thickness. This is a somewhat surprising result, which suggests that a transition layer may exist between the substrate and good quality a-Si. This transition layer may arise from either a gettering of impurities during the growth of the first

Figure 5

Relative Photoluminescence Efficiency
of DC(C), DC(G) and RF(A) a-Si:H films

micron or so of the film, or from defects induced by the substrate which can also be expected to reduce within the first micron or so. This latter hypothesis is consistent with the behavior of other heteroepitaxial semiconducting films.(13)

During this quarter, we have also observed excellent, dispersion-free electron transits in a-Si. Figure 6 shows a typical oscilloscope trace. By plotting $1/t$ vs. voltage, we obtain an excellent straight-line (See Figure 7), passing close to the origin, indicating that we are observing true transit-times in our experiments and not some artifact. The highest value of the electron drift mobility in our samples is $\mu_n \sim 0.8 \text{ cm}^2/\text{V-sec}$, as high as the best reported,(14) and significantly higher than the results from other groups.(15)

Table I

Mobility Data on a-Si:H

Sample #	Thickness (μm)	Mobility $\text{cm}^2/\text{V-sec}$	Growth Rate ($\text{\AA}/\text{sec}$)
80/320	4.7 - 4.9	0.46 - 0.48	6.0
80/321	5.7 - 6.0	0.7 - 0.87	8.1
80/322	1.21	Dispersive	1.55
80/393	1.46	Dispersive	4.1
80/394	4.9	0.7	6.3
80/395	8.7	0.5	5.14

All samples prepared from pure SiH_4 (epitaxial grade).
 $T = 350^\circ\text{C}$, $p = 500 \mu\text{m}$, RF (anodic, -50V) films.
 (Sample 320 prepared at 300°C).

Figure 6

Oscilloscope Trace of Transient
Current for Drift Mobility Experiment

Figure 7

IEC81041

Reciprocal of transit time vs. voltage
from drift mobility experiment

III. Device Fabrication and Analysis

We have continued work on nip/metal devices. Two kinds of devices have been made, a grid device with the geometry described in the previous quarter's report, and a transparent metal film (TMF) device. The metal contact is usually W. See Figure 8. The active area of the grid device is 0.41 cm^2 and the active area of the TMF device varies from $0.18 - 0.24 \text{ cm}^2$, depending upon the width of the bussbar. A major advantage of the TMF device is that handling is minimized (no etching of metal unlike the grid device), an important consideration for increasing the yield.

During this quarter, we have achieved the following results.

1. Short-circuit current. High internal J_{sc} have been achieved. On the TMF device, with a measured 42% reflection and 20% absorption in the metal layer, we obtain external current of $\sim 5.6 \text{ mA/cm}^2$, (at 100 mW/cm^2) under ELH lamp simulation. This corresponds to $\sim 14.0 \text{ mA/cm}^2$ internal current after allowing for the measured reflection and absorption loss in TMF film. A typical high current device $I(V)$ curve is shown in Figure 9.
2. Open-circuit voltage. High V_{oc} have also been achieved on the devices. ($\sim 820 \text{ mV}$). A device showing high V_{oc} is shown in Figure 10.
3. Fill-factor. Generally speaking, the fill-factors are low, 45-55%. There are 3 causes for the poor fill-factors.
 - i) High series resistance. A typical R_{series} in our cells is $> 50 \Omega\text{-cm}^2$. Such a high series resistance can lead to a significant loss in both short

Figure 8
Thin Metal film (TMF) Nip Cell

Figure 9: Device with High Internal Current

Figure 10: Device with High V_{oc}

circuit current and fill-factor. The loss in fill-factor can exceed 40% for such high series resistance.

ii) High shunt conductance. Our diodes do not generally suffer from high shunt conductance. Typically $R_{sh} > 10^3 \Omega\text{-cm}^2$. Such a high R_{sh} would lead to a loss of only 8% in fill factor.

iii) Depletion layer shrinkage. As the diode goes into forward bias, the junction depletion regions shrink. Hence, there is a longer neutral region through which the carriers must diffuse, which would lead to a loss in current with voltage bias. Thus, the $I(V)$ characteristic would become softer, i.e. a loss in fill-factor. During the next quarter, we want to study this phenomenon in detail so as to identify its contribution.

4. Influence of substrate. We have used two types of substrates, 7059 coated with Ti, and mechanically polished stainless steel. The following trends have been observed on these substrates.

i) The voltages in samples deposited on glass/metal substrates are always higher than on stainless steel. Typically, we obtain 750 - 820 mV on metallized glass, but 680 - 790 mV on stainless steel. We do not yet understand these results.

ii) The series resistance is usually lower on stainless steel substrates. Typically, $R_{series} \approx 50 \Omega\text{-cm}^2$ on stainless steel, but $\sim 100 \Omega\text{-cm}^2$ on metallized glass. Part of the increase in R_{series} is clearly due to the sheet resistance of the metal films ($\sim 50 \Omega/\square$). Efforts are underway to reduce this series resistance.

iii) The shunt resistance depends critically upon the thickness of the back p+ contact layer. (The layer adjacent to the metal substrate). In particular, 2-3 μm of p+ layer assures very low shunt conductance, and also assures high V_{OC} and J_{SC} . Once again, in common with mobility studies described in Section II, increasing the thickness of the device seems to improve all the electronic properties. We do not yet understand this behavior.

5. Influence of temperature and pressure. We find that deposition temperature and pressure have the following influences.

i) Increasing the deposition temperature of the back p+ layer seems to reduce series resistance. In particular, temperatures of 425 - 450 C seem beneficial for reducing R_{series} . This result can be explained by the fact that the conductivity of the p+ layer increases with increasing temperature as reported during the previous quarter⁽¹⁶⁾.

ii) A temperature of 300 - 350C seems desirable for depositing the i layer. This is consistent with the results of our subcontractors at Chicago who find that density of midgap states in a-Si:H increases drastically when one increases temperature beyond 350C.⁽¹⁷⁾

iii) Low SiH_4 pressures, < 150 - 200 μm , are necessary to produce the best diode n factors. We have obtained near-ideal diodes, with n factor = 1.2, with low pressure, low T (< 350C) deposition. An example is shown in Figure 11. Low SiH_4 pressures also reduce the production of Si dust by polymerization in the gas phase, thus avoiding pinholes due to dust inclusion in the film.

Figure 11
Plot of V_{oc} vs. $\log(I_{sc})$ for
a-Si:H nip cell

During the next quarter, we intend to study the influence of substrates and gas pressures more thoroughly so as to obtain better devices.

6. Quantum Efficiency. A major advance during this quarter has been the achievement of thin n^+ junction layers. Previously, thicker n^+ layers, ($t > 300 \text{ \AA}$) caused a severe loss in quantum efficiency in the blue and green regions of the spectrum. We have now successfully grown thin n^+ top junction layers ($\sim 150 \text{ \AA}$) which have led to substantial improvements in the QE in the blue-green regions of the spectrum. (See Figure 12). This has been one of the reasons for our improved currents.

During the next quarter, further improvement in our devices should result from close control of substrates, deposition conditions, thickness of different layers and anti-reflection coatings.

Figure 12: Spectral Response of Nip Cells
TMF W-Dot No AR Coating

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Appendix A

A DOPING-PRECIPITATED MORPHOLOGY IN PLASMA DEPOSITED a-Si:H

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A grossly inhomogeneous, noncolumnar morphology has been observed in doped, plasma-deposited hydrogenated amorphous silicon (a-Si:H) within critical ranges of the diborane to silane ratio in the gas phase. The diborane level can be as low as 5 ppm and depends both on the electrode self-bias potential and the growth rate. Undoped specimens prepared under the same deposition conditions have properties typical of device-grade a-Si:H. These morphology observations suggest a structural origin for some doping-dependent properties in a-Si:H.

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The widespread interest in hydrogenated amorphous silicon (a-Si:H) is the consequence of the remarkably low density of electronically active defects in suitably prepared material. The elucidation of these remaining defects is naturally a principal objective of research on a-Si:H, and in particular a dominant issue in this research is the relationship of the inhomogeneities which exist in the material to its defect-controlled properties. Electron microscopy (1) in conjunction with small-angle neutron and X-ray scattering (2) has shown the existence in undoped material of an anisotropic microstructure consisting of fine rods aligned with the film growth direction. This microstructure is associated with a columnar morphology in the film, and has been correlated with spin-density and luminescence efficiency (1) and with compositional heterogeneities (3).

In this letter we report our observations of a grossly inhomogeneous, noncolumnar morphology in a-Si:H which is precipitated by the use of low concentrations of diborane as a dopant gas ($[B_2H_6]/[SiH_4] \lesssim 5$ ppm). This morphology is observed under deposition conditions typical of device-grade a-Si:H (cf. Table I); undoped specimens prepared under otherwise identical conditions are featureless under scanning electron microscope examination. The sensitivity to doping of the electrical conductance and the photoconductance of a-Si:H has generally been understood using a simple substitutional model (4) in which a fraction of the dopant atoms become shallow donors or acceptors; this model excludes any effects of doping on the underlying microstructure of the material. While the present morphology observations alone do not rule out this substitutional model completely, they demonstrate that the plasma deposition process is strongly perturbed by the use of doping gases. They further suggest that the doping dependence of the electron

density of states reported in photoemission (5), and DLTS (6) measurements may have a structural origin, especially in light of the recent results which show that films which are featureless to morphological examination possess compositional heterogeneity (3).

The plasma deposition apparatus employed for the present studies is a capacitively coupled system of the type originally applied to a-Si:H by Knights (7). Specimens were deposited under the range of conditions listed in Table I. The parametrization used in this table is largely conventional; nonetheless several parameters require clarification. The gas pressures and flows indicate conditions before the plasma discharge is started. The terms cathode and anode for the hot RF electrode and the grounded electrode, respectively, are misnomers; both cathode and anode acquire a negative DC potential with respect to the plasma. These bias potentials were estimated from a simple approximation for the behavior of an RF plasma (8,9) using the measured RF and DC potentials between the cathode and anode:

$$V_a = -(V_{rf} + V_{ca})/2 \quad (1a)$$

$$V_c = -(V_{rf} - V_{ca})/2 \quad (1b)$$

where V_{RF} is the (positive) RF amplitude between the cathode and anode and V_{ca} is the DC potential between them. Specimens were normally deposited onto Corning, Inc. 7059 glass substrates held against the anode and cathode surfaces by stainless steel retaining plates; these plates have a significant influence on the deposition process which will be discussed subsequently.

The growth rates of anode and cathode specimens were essentially equal and were nearly proportional to the RF amplitude; growth rates ranged from 40 to 180 Å/m. The diborane doping level had less than a 20 percent effect on the growth rate over the doping range studied. No noticeable

effects of depletion of the SiH_4 gas during deposition were observed or expected from the flows and deposition rates used.

Scanning electron micrographs of the anode and cathode specimens obtained from two depositions of varying length are reproduced in Fig. 1. The anode specimens were visibly milky. The anode specimen micrograph for the thinner 0.5 micron specimen (Fig. 1(a)) exhibits a pebbled surface from which some material has flaked away, revealing a finer grained fracture surface. The cathode specimen was transparent, and little structure was observed with the scanning electron microscope (resolution 200 Å). Fracture surfaces of similar, transparent films were conchoidal. The micrograph of a substantially thicker (1 micron) anode specimen is reproduced in Fig. 1(c). Instead of coalescing with further growth the film has become more inhomogeneous, apparently reflecting an instability of the film growth process to formation of large nodules with a diameter of order 1 micron. We shall refer to this morphology as "agglomerative."

The deposition parameters which affected formation of this agglomerative morphology included the gas pressure, the doping level, the RF field amplitude, and the electrode bias relative to the plasma. The extent of dilution of SiH_4 in Ar did not have a noticeable effect on the film morphology between 0.01 to 0.5 dilution level. This result is not unexpected in light of the very weak influence of the dilution level on the film growth rate in the absence of SiH_4 depletion (11), but it contrasts with the substantial influence of dilution on columnar morphology (1). It is unclear to what extent these results on columnar morphology were influenced by SiH_4 depletion. The agglomerative morphology was observed both on glass and on Al foil substrates, though not necessarily in a given deposition. The morphology was

also observed on glass substrate areas with predeposited molybdenum or nichrome contacts.

The interplay of the RF amplitude and the boron doping level in precipitating the agglomerative morphology was investigated extensively under fixed conditions of gas pressure and flow, argon dilution, and substrate temperature; the results of this investigation are summarized in Fig. 2. The shaded regions indicate the presence of agglomerative morphology; twenty-one depositions distributed fairly evenly over the region within the dashed lines were used to prepare the figure. The anode and cathode DC potentials (relative to the plasma) presented on the nomogram to the right were calculated from the expressions given earlier. The actual potential on the insulating substrate surface need not be the same as the electrode potential. Occasionally some traces of the agglomerative morphology were found in specimens somewhat outside the contours. In these regions the morphology varied widely over the surface of the electrode. Elliptical cloudy regions about the center of the circular electrode were found in which the peripheral regions were transparent and showed less pronounced structure under the scanning electron microscope. These patterns are attributed to variations of the RF field over the area of the electrode.

The most striking attribute of the data summarized in Fig. 2 is the limited character of the regions in which the agglomerative morphology is present; on both electrodes this morphology can be suppressed by variations in either direction of the doping or RF amplitude. This limited character should be contrasted with the conditions under which columnar morphology has been observed in undoped material: This morphology is uniformly enhanced as either RF power or Ar dilution are increased towards levels at which depletion of the SiH_4 gas occurs. The agglomerative morphology may

thus mark a transition between two different growth domains of a-Si:H, presumably with relatively simple underlying microstructures, rather than being indicative of any single microstructure.

The observations summarized in Fig. 2 were made using the metal retaining plates described earlier. This plate is unnecessary for retaining specimens on the bottom (anode) electrode; removal of the retaining plate under deposition conditions expected to produce anode specimen agglomerative morphology ($1.5 \times 10^{-5} [\text{B}_2\text{H}_6]/[\text{SiH}_4]$, 225 V RF amplitude) resulted in transparent specimens with a homogeneous morphology. Most striking of all was a deposition onto a glass substrate which had cracked neatly into two pieces as the cathode retaining plate was screwed down. The relatively loose piece had a transparent film, and the tightly secured piece a cloudy one. These puzzling effects are speculatively attributed to the role of insulating substrate biases which differ from the metal electrode bias. The presumption that potentials measured on a metal electrode are identical with those on an insulating surface is known to be in error from RF sputtering experiments (11). We ascertained that the differences were not caused by variations in substrate temperatures.

The implications of the agglomerative morphology reported here for the underlying nucleation and growth mechanisms in a-Si:H are not yet understood. However, the noncolumnar character of this morphology indicates that the film's underlying microstructure does not consist of the fine rods aligned with the growth direction found in some undoped a-Si:H specimens and which were previously suggested as a universal microstructure in plasma deposited a-Si:H (1). This new morphology further emphasizes the need both

for additional studies of a-Si:H film growth and nucleation in general and for a better understanding of the effects of doping gases on these processes.

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Table I. Deposition Conditions

Electrode Separation	2.5cm
Cathode Diameter	6.7cm
Anode Diameter	7.1cm
$[B_2H_6]/[SiH_4]$	$0-1.5 \times 10^{-4}$
SiH_4 Dilution	1-50% in Ar
Gas Flow	15-60 sccm
Gas Pressure	100-300 mTorr
Substrate Temperature	230-330C
RF Frequency	13.56 MHz
RF Amplitude	80-370V
RF Power	0.5-10W
Anode Self-Bias	-25 - -110V
Cathode Self-Bias	-55 - -260V

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Figure Captions

- Figure 1: Scanning electron micrographs of doped (a) 0.5 micron thick anode specimen, (b) 0.5 micron thick cathode specimen, (c) 1 micron thick anode specimen for $V_{rf} = 220$ V, $[B_2H_6]/[SiH_4] = 1.5 \times 10^{-5}$. Other deposition conditions: $[SiH_4]/[Ar] = 0.1$, gas flow 30 sccm, gas pressure 150 mTorr, electrode temperature 260 C. Specimens were coated with a 200 Å Au-Pd film to reduce charging.
- Figure 2: Map of occurrence of agglomerative morphology as RF amplitude and B_2H_6 doping level are varied. Other deposition conditions are the same as for Fig. 1. V_c and V_a are the cathode and anode DC potentials relative to the plasma, respectively.

2 μ m

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